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(54) **Lubricating oil compositions and concentrates and the use thereof**

Schmierölszusammensetzungen, Konzentrate und ihre Verwendung

Compositions d'huile lubrifiante et de concentrés et leur utilisation

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EP-A- 0 271 937 EP-A- 0 359 522
EP-A- 0 384 639 EP-A- 0 454 380
GB-A- 1 061 494 US-A- 3 502 677
US-A- 4 842 755

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Description

This invention relates to oleaginous compositions of enhanced performance characteristics, to additive concentrates for enhancing the performance characteristics of oleaginous base fluids (e.g., lubricants and functional fluids), and to methods of achieving such enhanced performance characteristics.

Over the years the demand for performance improvements in lubricating oils and functional fluids has persisted and, if anything, progressively increased. For example, lubricating oils for use in internal combustion engines, and in particular, in spark-ignition and diesel engines, are constantly being modified and improved to provide improved performance. Various organizations including the SAE (Society of Automotive Engineers), the ASTM (formerly the American Society for Testing Materials) and the API (American Petroleum Institute) as well as the automotive manufacturers continually seek to improve the performance of lubricating oils. Various standards have been established and modified over the years through the efforts of these organizations. As engines have increased in power output and complexity, and in many cases decreased in size, the performance requirements have been increased to provide lubricating oils that will exhibit a reduced tendency to deteriorate under conditions of use and thereby to reduce wear and the formation of such undesirable deposits as varnish, sludge, carbonaceous materials and resinous materials which tend to adhere to various engine parts and reduce the operational efficiency of the engine.

Current objectives include the development of additive formulations and lubricant compositions, especially crankcase lubricants and crankcase lubricant additive packages, capable of achieving these stringent performance requirements without requiring use of increased amounts of metal-containing components, such as zinc dihydrocarbyl dithiophosphates. Indeed, if possible, it is desired to achieve these stringent performance requirements with reduced amounts of such metal-containing components. Still another desirable objective is to provide additive formulations and lubricant compositions which exhibit good compatibility with elastomeric substances utilized in the manufacture of seals, gaskets, clutch plate facings, diaphragms, and like parts. Unfortunately, commonly used additives containing basic nitrogen constituents tend to cause excessive degradation of such elastomers when oils containing such additives come in contact with such elastomers during actual service conditions.

There are literally hundreds, if not thousands, of patent disclosures describing attempts (some more successful than others) to improve the performance characteristics of oils of lubricating viscosity. The following is but a small selection from this vast body of literature: U.S. Pat. Nos. 3,087,936;

3,184,411;	3,185,645;	3,235,497;	3,254,025;
3,265,618;	3,281,428;	3,282,955;	3,284,410;
3,324,032;	3,325,567;	3,338,832;	3,344,069;
3,403,102;	3,502,677;	3,511,780;	3,513,093;
3,533,945;	3,623,985;	3,718,663;	3,865,740;
3,950,341;	3,991,056;	4,097,389;	4,234,435;
4,338,205;	4,428,849;	4,554,086;	4,615,826;
4,634,543;	4,648,980;	4,747,971;	4,857,214;

and 4,873,004.

United States Patent 3,502,677 describes substituted polyamines which are useful in lubricants as dispersants or detergents to prevent sludge and deposit formation as lubricating oils deteriorate. The polyamine may be formed by reaction of an alkylene polyamine with a hydrocarbon substituted succinic acid-producing compound followed by post-treatment with a phosphorus acid-producing compound. The latter may be selected from "phosphorous acids" but there is no disclosure or suggestion of post-treatment using phosphorous acid (H_3PO_3).

EP-A-454,380 relates to a lubricating oil containing a minor amount of dispersant which is a mixture of succinimide and Mannich-type dispersants. The succinimide dispersant may be post-treated with a boron compound, a phosphorus compound, maleic anhydride, and combinations thereof. There is no disclosure of post-treatment of the dispersant with H_3PO_3 . EP-A-454,380 has a priority date earlier than that claimed by the present application but was not published until after the priority date of the present application. It is citable against the present application under Article 54(3) EPC.

EP-A-359,522 in the name of the present applicants, is concerned with the provision of lubricant additives which have improved oxidation performance and protection for rubber seals. The additive is an oil-soluble reaction product of an inorganic phosphorus acid or anhydride with a boron compound and an ashless dispersant which contains basic nitrogen and/or a free hydroxyl group. Phosphorous acid is referred to as being the preferred inorganic acid. However, the discussion of the various tests conducted in EP-A-359,522 makes clear that it is not necessary to include in lubricants containing the additive a metal hydrocarbyl dithiophosphate or dithiocarbamate performance improver. Quite acceptable results with respect to oxidation thermal stability and wear resistance are achieved in the absence of the metal-containing component.

EP-A-271,37 describes a lubricant additive having improved dispersency properties. The additive is a polyolefin-substituted succinimide which may be post-treated and a large number of possible reagents suitable for post-treatment are identified. The only phosphorus-containing reagents referred to are phosphorus sulfides, phosphorus oxides and phos-

phoric acid.

This invention provides additive systems capable of imparting enhanced performance characteristics to natural and synthetic oils of lubricating viscosity. In addition, this invention makes it possible to achieve such enhanced performance with additive systems containing reduced amounts of metal-containing performance enhancers such as metal dithio-
 5 phosphates (e.g., zinc dialkyldithiophosphates) and/or metal dithiocarbamates.

In accordance with this invention there is provided in one of its embodiments a lubricant or functional fluid composition comprising a major proportion of at least one oil of lubricating viscosity and a minor proportion of the components of an additive concentrate composition comprising: a) one or more oil-soluble metal hydrocarbyl dithiophosphates or dithiocarbamates; and b) one or more oil-soluble boron-free additive compositions formed by heating (i) at least one
 10 boron-free oil-soluble ashless dispersant comprising at least one acyclic hydrocarbyl-substituted succinimide formed from a mixture of ethylene polyamines having an approximate overall composition falling in the range corresponding to diethylene triamine to pentaethylene hexamine, and wherein the succinimide contains basic nitrogen, with (ii) phosphorus acid, H_3PO_3 , such that a liquid boron-free phosphorus-containing composition is formed. The cooperation between components a) and b) of such compositions makes it possible to achieve performance levels (reduction in sludge formation and/or deposition and reduction in wear in gears and/or other relatively moveable metal surfaces in contact with
 15 each other) normally achieved, if at all, by higher concentrations of component a). Moreover, these performance levels can be maintained for long periods of time despite the well-known relatively low thermal stability of compounds such as the zinc dihydrocarbyl dithiophosphates. Preferably, the total amount of components a) and b) is in the range 0.3% to 17% by weight based on the total weight of the composition.

Another advantage of this invention is that certain preferred combinations of components a) and b) can exhibit good compatibility toward elastomers commonly employed in the manufacture of seals or gaskets, clutch plate facings and diaphragms, such as nitrile rubbers, fluoroelastomers, and silicone-type elastomers. In other words, such elastomers are not subjected to excessive degradation when in contact under actual service conditions with a preferred lubricant or functional fluid composition of this invention containing particular combinations of components a) and b), which combinations are thus preferred because of this advantageous property which they possess and exhibit in the base oil. To
 25 realize these beneficial properties the overall sulfur content of the finished lubricant or functional fluid composition should be typically kept below 1% and most preferably below 0.3% based on the total weight of the finished lubricant or functional fluid composition.

Another embodiment of this invention involves the discovery, inter alia, that basic alkali metal-containing and/or basic alkaline earth metal-containing detergents of the types generally known to be useful in oleaginous fluids (e.g., overbased sulfonates, overbased phenates, overbased sulfurized phenates, overbased salicylates and overbased sulfurized salicylates) can serve a dual role in the compositions of this invention. Besides contributing detergency to the compositions, such metal compounds can serve to reduce corrosive attack on so-called "yellow metals" such as copper and bronze. Detergents of the foregoing types having a total base number (TBN) of at least 50 are preferably utilized
 35 in the practice of this embodiment of the invention. TBN is determined in accordance with ASTM D-2896-88.

Accordingly, the additive concentrate composition preferably further comprises, as component c), at least one oil-soluble alkali or alkaline earth metal-containing detergent, preferably a sulfonate detergent, the relative proportions of the components of said composition being such that per atom of phosphorus in said component (b), there are from 0.15 to 10 atoms of metal as component (a) and from 0.05 to 150 atoms of alkali or alkaline earth metal as component (c).

Additive concentrates comprising at least components a) and b) above, and preferably additionally containing component c), i.e., one or more suitably basic, oil-soluble alkali metal-containing and/or alkaline earth metal-containing detergents, constitute additional embodiments of this invention. Such concentrates contain a minor proportion of at least one diluent oil of lubricating viscosity (usually a process oil) and a major proportion of the active ingredients or components utilized in forming the additive concentrate.

It has been found, quite surprisingly, that in order to achieve optimum performance as regards minimal corrosive attack on yellow metals such as copper, the order in which components a), b) and c) are blended together should be properly sequenced. In particular, in order to achieve minimal copper corrosivity, components a) and b) should not be premixed in the absence of component c). Thus in situations where optimum compatibility with copper is necessary or desirable, it is preferable, in forming any additive concentrate in which components a), b) and c) are used, to preblend components b) and c) before mixing with component a). Likewise, in forming a lubricant or functional fluid by adding the components separately into the oil (rather than blending into the oil an additive concentrate of this invention formed in the manner specified in this paragraph which is most preferred), it is preferable to either add a preblend of components b) and c) to the oil before blending component a) in the oil, or to separately blend components b) and c) into the oil (in either order) before blending component a) into the oil. Accordingly, the blending procedures and modes of addition set forth in this paragraph constitute still additional preferred embodiments of this invention.

According to another embodiment of this invention the additive concentrate composition further comprises, as component d), one or more oil-soluble or oil-dispersible boron-containing compound, the relative proportions of the components of said composition being such that per atom of phosphorus in said component (b), there are from 0.15 to 10

atoms of metal as component (a) and from 0.15 to 200 atoms of boron as component (d).

Such compositions are of particular effectiveness under conditions where scuffing wear is likely to be encountered. Although it is preferable to include component c) in these compositions, it is possible to achieve satisfactory results with compositions comprising components a) , b), and d), and devoid of component c). Thus these latter compositions form yet another embodiment of this invention.

Likewise, additive concentrates which comprise the above components a), b), c), and d), and additive concentrates which comprise the above components a), b) and d) form still additional embodiments of this invention.

Among the preferred embodiments of this invention are oleaginous compositions and additive concentrates in which component a) is at least one oil-soluble metal hydrocarbyl dithiophosphate (preferably a zinc hydrocarbyl dithiophosphate and most preferably a zinc dialkyl dithiophosphate), and in which the relative proportions of components a) and b) are such that the atom ratio of phosphorus in the form of component a) to phosphorus in the form of component b), respectively, falls in the range of 5:1 to 0.1:1 and more preferably in the range of 4:1 to 1:1. Particularly preferred are compositions of these types which additionally contain component c) in an amount such that the atom ratio of total metal in the form of component a) to total metal in the form of component c), respectively, falls in the range of 0.01:1 to 10:1 (and more preferably in the range of 0.1:1 to 4:1). Especially preferred are lubricants and functional fluids containing components a), b), and c) proportioned as specified in this paragraph wherein the total content of metals in the form of components a) and c) is in the range of 0.01 to 3, preferably in the range of 0.05 to 1.8, and most preferably in the range of 0.1 to 1.0 weight percent of metals based on the total weight of the lubricant composition or functional fluid composition. Despite their low level of "ash" or metal-containing components, such lubricant and functional fluid compositions can provide a high level of performance.

In order to satisfy the stringent specification requirements to qualify for top-grade crankcase lubricating oils, a combination of at least one oil-soluble antioxidant e) and oil-soluble corrosion inhibitor f) is preferably included in the compositions of this invention, such that said lubricant composition satisfies (1) the requirements of the Sequence IID, Sequence IIIE, and Sequence VE procedures of the American Petroleum Institute; and/or (2) the requirements of the L-38 Test Procedure of the American Petroleum Institute; and/or (3) the requirements of the Caterpillar® 1G(2) and/or the 1H(2) Test Procedure. In this way, the enhanced performance (e.g., control of sludge, deposit and varnish formation and of wear of contacting metal parts) made possible by this invention can be maintained while at the same time satisfying specification requirements associated with oxidation and corrosion inhibition.

The Sequence IID procedure is as set forth in ASTM STP 315H Part 1, including any and all amendments detailed by the Information Letter System (up to November 1, 1990). The Sequence IIIE procedure is as set forth in ASTM Research Report: D-2:1225 of April 1, 1988 including any and all amendments detailed by the Information Letter System (up to November 1, 1990). The Sequence VE procedure is as set forth in ASTM Sequence VE Test Procedure, Seventh Draft, May 19, 1988, including any and all amendments detailed by the Information Letter System (up to November 1, 1990). The L-38 procedure is as set forth in ASTM D-5119, including any and all amendments detailed by the Information Letter System (up to November 1, 1990). The Caterpillar® 1G(2) procedure is as set forth in ASTM STP 509A, Part 1, including any and all amendments detailed by the Information Letter System (up to November 1, 1990). The Caterpillar® 1H(2) procedure is as set forth in ASTM STP 509A, Part 2, including any and all amendments detailed by the Information Letter System (up to November 1, 1990). Additive concentrates which comprise at least components a), b), c), d) and e) as set forth above, and which when blended with a base oil of lubricating viscosity provide a lubricant satisfying the foregoing Sequence IID, IIIE, and VE procedures; and/or the L-38 procedure; and/or at least one of the Caterpillar® 1G(2) and Caterpillar® 1H(2) procedures constitute still additional especially preferred embodiments of this invention. The most preferred embodiments are lubricant compositions and additive concentrates which satisfy the requirements of all of the Sequence IID, Sequence IIIE, Sequence VE, L-38, Caterpillar® 1G(2) and Caterpillar® 1H(2) procedures.

Among the most preferred embodiments of this invention are oleaginous fluids wherein component a) is composed of one or more oil-soluble zinc dihydrocarbyl dithiophosphates, wherein components a) and b) are proportioned such that the atom ratio of phosphorus in the form of component a) to phosphorus in the form of component b), respectively, falls in the range of 4:1 to 1:1, and wherein the phosphorus content of such fluids is in the range of 0.05 to 0.15% by weight of the total composition, especially where such fluids additionally contain at least one oil-soluble alkali or alkaline earth metal-containing detergent having a TBN of at least 50, preferably above 100, more preferably above 200, and most preferably above 300.

More particularly the invention provides lubricant or functional fluid compositions having a total halogen content, if any, not exceeding 100 ppm, and additive concentrates which, if dissolved in a halogen-free base oil, at a concentration of 10% by weight, yield an oleaginous composition in which the total halogen content, if any, is 100 ppm or less. Lubricant or functional fluid compositions of the invention may contain at least about 0.03% of phosphorus, preferably at least about 0.04% of phosphorus, more preferably at least about 0.05% of phosphorus, and most preferably at least about 0.06% of phosphorus, as component (b).

The lubricant or functional fluid compositions of the invention are especially useful when used in a mechanical mechanism, e.g. an internal combustion engine, which may be a spark-ignition (gasoline) engine or a compression-ig-

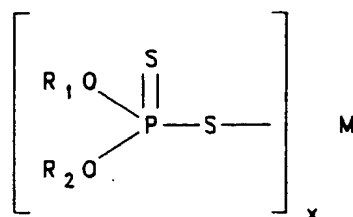
nitron (diesel) engine, or a vehicular transmission, which may be automatic or manual, or a gear box, in contact with an elastomeric material such as a fluoroelastomer.

Component a)

In essence, there are two general categories of additives which may be used singly or in combination with each other as component a) in the practice of this invention. One type is comprised of oil-soluble metal hydrocarbyl dithiophosphates. The other is comprised of oil-soluble metal hydrocarbyl dithiocarbamates.

Type 1 - Metal hydrocarbyl dithiophosphates.

As is well known, metal hydrocarbyl dithiophosphates are usually prepared by reacting phosphorus pentasulfide with one or more alcohols or phenolic compounds or diols to produce a hydrocarbyl dithiophosphoric acid which is then neutralized with one or more metal-containing bases. When a monohydric alcohol or phenol is used in this reaction, the final product is a metal dihydrocarbyl dithiophosphate. On the other hand, when a suitable diol (e.g., 2,4-pentanediol) is used in this reaction, the final product is a metal salt of a cyclic hydrocarbyl dithiophosphoric acid. See, for example, U.S. Pat. No. 3,089,850. Thus typical oil-soluble metal hydrocarbyl dithiophosphates used as component a) may be represented by the formula



where R_1 and R_2 are, independently, hydrocarbyl groups or taken together are a single hydrocarbyl group forming a cyclic structure with the phosphorus and two oxygen atoms, preferably a hydrocarbyl-substituted trimethylene group of sufficient carbon content to render the compound oil soluble, M is a metal, and x is an integer corresponding to the valence of M. The preferred compounds are those in which R_1 and R_2 are separate hydrocarbyl groups (i.e., the metal dihydrocarbyl dithiophosphates). Usually the hydrocarbyl groups of the metal dihydrocarbyl dithiophosphates will contain no more than 50 carbon atoms each although even higher molecular weight hydrocarbyl groups can be present in the compound. The hydrocarbyl groups include cyclic and acyclic groups, both saturated and unsaturated, such as alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, cycloalkylalkyl, aralkyl, and the like. It will be understood that the hydrocarbyl groups may contain elements other than carbon and hydrogen provided such other elements do not detract from the predominantly hydrocarbonaceous character of the hydrocarbyl group. Thus the hydrocarbyl groups may contain ether oxygen atoms, thioether sulfur atoms, secondary or tertiary amino nitrogen atoms, and/or inert functional groups such as esterified carboxylic groups, keto groups, thioketo groups, and the like.

The metals present in the oil-soluble metal dihydrocarbyl dithiophosphates and oil-soluble metal cyclic hydrocarbyl dithiophosphates include such metals as lithium, sodium, potassium, copper, magnesium, calcium, zinc, strontium, cadmium, barium, mercury, aluminum, tin, lead, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, ruthenium, etc., as well as combinations of two or more such metals. Of the foregoing, the salts containing group II metals, aluminum, lead, tin, molybdenum, manganese, cobalt, and/or nickel, are preferred. The dihydrocarbyl dithiophosphates of zinc and copper are particularly preferred, with the zinc salts being the most preferred type of compound for use as component a).

The phosphorodithioic acids from which the metal salts are formed can be prepared by the reaction of 4 moles of one or more alcohols (cyclic or acyclic) or one or more phenols or mixture of one or more alcohols and one or more phenols (or 2 moles of one or more diols) per mole of phosphorus pentasulfide, and the reaction may be carried out within a temperature range of from 50 to 200°C. The reaction generally is completed in 1 to 10 hours. Hydrogen sulfide is liberated during the reaction.

Another method for the preparation of the phosphorodithioic acids involves reaction of one or more alcohols and/or one or more phenols with phosphorus sesquisulfide in the presence of sulfur such as is described in PCT International Publication No. WO 90/07512. This reaction is conducted at an elevated temperature, preferably in the range of 85-150°C with an overall atomic P:S ratio of at least 2.5:1.

The alcohols used in forming the phosphorodithioic acids by either of the above methods are preferably primary alcohols, or secondary alcohols. Mixtures thereof are also suitable. The primary alcohols include propanol, butanol, isobutyl alcohol, pentanol, 2-ethyl-1-hexanol, isooctyl alcohol, nonanol, decanol, undecanol, dodecanol, tridecanol, tet-

radecanol, octadecanol, eicosanol, and the like. The primary alcohols may contain various substituent groups such as halogen atoms, nitro groups, etc., which do not interfere with the desired reaction. Among suitable secondary alcohols are included 2-butanol, 2-pentanol, 3-pentanol, 2-hexanol, 5-methyl-2-hexanol, and the like. In some cases, it is preferable to utilize mixtures of various alcohols, such as mixtures of 2-propanol with one or more higher molecular weight primary alcohols, especially primary alcohols having from 4 to 13 carbon atoms in the molecule. Such mixtures preferably contain at least 10 mole percent of 2-propanol, and usually will contain from 20 to 90 mole percent of 2-propanol. In one preferred embodiment, the alcohol comprises 30 to 50 mole percent of 2-propanol, 30 to 50 mole percent isobutyl alcohol and 10 to 30 mole percent of 2-ethyl-1-hexanol.

Other suitable mixtures of alcohols include 2-propanol/butanol; 2-propanol/2-butanol; 2-propanol/2-ethyl-1-hexanol; butanol/2-ethyl-1-hexanol; isobutyl alcohol/2-ethyl-1-hexanol; and 2-propanol/tridecanol.

Cycloaliphatic alcohols suitable for use in the production of the phosphorodithioic acids include cyclopentanol, cyclohexanol, methylcyclohexanol, cyclooctanol, borneol and the like. Preferably, such alcohols are used in combination with one or more primary alkanols such as butanol, isobutyl alcohol, or the like.

Illustrative phenols which can be employed in forming the phosphorodithioic acids include phenol, o-cresol, m-cresol, p-cresol, 4-ethylphenol, 2,4-xyleneol, and the like. It is desirable to employ phenolic compounds in combination with primary alkanols such as propanol, butanol, hexanol, or the like.

Other alcohols which can be employed include benzyl alcohol, cyclohexenol, and their ring-alkylated analogs.

When mixtures of two or more alcohols and/or phenols are employed in forming the phosphorodithioic acid, the resultant product will normally comprise a mixture of three or more different dihydrocarbyl phosphorodithioic acids, usually in the form of a statistical distribution in relation to the number and proportions of alcohols and/or phenols used.

Illustrative diols which can be used in forming the phosphorodithioic acids include 2,4-pentanediol, 2,4-hexanediol, 3,5-heptanediol, 7-methyl-2,4-octanediol, neopentyl glycol, 2-butyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, and the like. The preparation of the metal salts of the dihydrocarbyl dithiophosphoric acids or the cyclic hydrocarbyl dithiophosphoric acids is usually effected by reacting the acid product with a suitable metal compound such as a metal carbonate, metal hydroxide, metal alkoxide, metal oxide, or other appropriate metal salt. Simply mixing and heating such reactants is normally sufficient to cause the reaction to occur and the resulting product is usually of sufficient purity for use in the practice of this invention. Typically, the salts are formed in the presence of a diluent such as an alcohol, water or a light mineral oil. Neutral salts are prepared by reacting one equivalent of metal oxide or hydroxide with one equivalent of the acid. Basic metal salts are prepared by adding an excess (i.e., more than one equivalent) of the metal oxide or hydroxide with one equivalent of the dihydrocarbyl phosphorodithioic acid or cyclic hydrocarbyl phosphorodithioic acid.

Illustrative metal compounds which may be used in such reactions include calcium oxide, calcium hydroxide, silver oxide, silver carbonate, magnesium oxide, magnesium hydroxide, magnesium carbonate, magnesium ethoxide, zinc oxide, zinc hydroxide, strontium oxide, strontium hydroxide, cadmium oxide, cadmium hydroxide, cadmium carbonate, barium oxide, aluminum oxide, aluminum propoxide, iron carbonate, copper hydroxide, lead oxide, tin butoxide, cobalt oxide, nickel hydroxide, manganese oxide, and the like.

In some cases, incorporation of certain ingredients such as small amounts of metal acetate or acetic acid in conjunction with the metal reactant will facilitate the reaction and provide an improved product. For example, use of up to 5% of zinc acetate in combination with the required amount of zinc oxide tends to facilitate the formation of zinc dihydrocarbyl dithiophosphates.

Examples of useful metal salts of dihydrocarbyl dithiophosphoric acids, and methods for preparing such salts are found in the prior art such as for example, U.S. Pat. Nos. 4,263,150; 4,289,635; 4,308,154; 4,322,479; 4,417,990; and 4,466,895.

Generally speaking, the preferred types of metal salts of dihydrocarbyl dithiophosphoric acids are the oil-soluble metal salts of dialkyl dithiophosphoric acids. Such compounds generally contain alkyl groups having at least three carbon atoms, and preferably the alkyl groups contain up to 10 carbon atoms although as noted above, even higher molecular weight alkyl groups are entirely feasible. A few illustrative zinc dialkyl dithiophosphates include zinc diisopropyl dithiophosphate, zinc dibutyl dithiophosphate, zinc diisobutyl dithiophosphate, zinc di-sec-butyl dithiophosphate, the zinc dipentyl dithiophosphates, the zinc dihexyl dithiophosphates, the zinc diheptyl dithiophosphates, the zinc dioctyl dithiophosphates, the zinc dinonyl dithiophosphates, the zinc didecyl dithiophosphates, and the higher homologs thereof. Mixtures of two or more such metal compounds are often preferred for use such as metal salts of dithiophosphoric acids formed from mixtures of isopropyl alcohol and secondary butyl alcohol; isopropyl alcohol, isobutyl alcohol, and 2-ethylhexyl alcohol; isopropyl alcohol, butyl alcohol, and pentyl alcohol; isobutyl alcohol and octyl alcohol; and the like. If desired, the metal dihydrocarbyl dithiophosphate additives of the type described above may be treated with an epoxide to form an adduct. In general, the most suitable metal dihydrocarbyl dithiophosphates useful in forming such adducts are the zinc dihydrocarbyl dithiophosphates. The epoxides comprise alkylene oxides and arylalkylene oxides. Typical alkylene oxides which may be used include alkylene oxides having up to 8 carbon atoms in the molecule, such as ethylene oxide, propylene oxide, 1,2-butene oxide, trimethylene oxide, tetramethylene oxide, butadiene monoepoxide, 1,2-hexene oxide, epichlorohydrin, and the like. The arylalkylene oxides are exemplified by styrene oxide. Other suitable

epoxides include, for example, butyl 9,10-epoxystearate, epoxidized soybean oil, epoxidized tung oil, and epoxidized styrene-butadiene copolymer. Procedures for preparing epoxide adducts are known and are reported, for example, in U. S. Pat. No. 3,390,082.

The adduct may be obtained by simply mixing the metal phosphorodithioate and the epoxide. The reaction is usually exothermic and may be carried out within wide temperature limits from 0°C to 300°C. Because the reaction is exothermic, it is best carried out by adding one reactant, usually the epoxide, in small increments to the other reactant in order to obtain convenient control of the temperature of the reaction. The reaction may be carried out in a solvent such as benzene, mineral oil, naphtha, or n-hexene.

The chemical structure of the adduct is not known. The adducts obtained by the reaction of one mole of the phosphorodithioate with from 0.25 mole to 5 moles, usually up to 0.75 mole or 0.5 mole of a lower alkylene oxide, particularly ethylene oxide and propylene oxide, are the preferred adducts.

Another type of metal dihydrocarbyl phosphorodithioate additives contemplated as useful as component a) in the compositions of this invention comprises mixed-acid metal salts of a combination of (a) at least one phosphorodithioic acid of the formula $(RO)(R'O)PSSH$, as exemplified above (R and R' being, independently, hydrocarbyl groups (or taken together, a single hydrocarbyl group forming a cyclic moiety with the two oxygen atoms and the phosphorus atom) of sufficient carbon content to render the salt soluble in lubricating oil), and (b) at least one aliphatic or alicyclic carboxylic acid. The carboxylic acid may be a monocarboxylic or polycarboxylic acid, usually containing from 1 to 3 carboxy groups and preferably only one. It may contain from 2 to 40, preferably from 2 to 20 carbon atoms, and advantageously 5 to 20 carbon atoms. The preferred carboxylic acids are those having the formula R^3COOH , wherein R^3 is an aliphatic or alicyclic hydrocarbon-based radical preferably free from acetylenic unsaturation. Suitable acids include the butanoic, pentanoic, hexanoic, octanoic, nonanoic, decanoic, dodecanooctadecanoic and eicosanoic acids, as well as olefinic acids such as oleic, linoleic, and linolenic acids and linoleic acid dimer. For the most part, R^3 is a saturated aliphatic group and especially a branched alkyl group such as the isopropyl or 3-heptyl group. Illustrative polycarboxylic acids are succinic, alkyl- and alkenylsuccinic, adipic, sebacic and citric acids.

The mixed-acid metal salts may be prepared by merely blending a metal salt of a phosphorodithioic acid with a metal salt of a carboxylic acid in the desired ratio. The ratio of equivalents of phosphorodithioic to carboxylic acid salts is between 0.5:1 and 200:1. Advantageously, the ratio can be from 0.5:1 to 100:1, preferably from 0.5:1 to 50:1, and more preferably from 0.5:1 to 20:1. Further, the ratio can be from 0.5:1 to 4.5:1, preferably 2.5:1 to 4.25:1. For this purpose, the equivalent weight of a phosphorodithioic acid is its molecular weight divided by the number of -PSSH groups therein, and that of a carboxylic acid is its molecular weight divided by the number of carboxy groups therein.

A second and preferred method for preparing the mixed-acid metal salts useful in this invention is to prepare a mixture of the acids in the desired ratio and to react the acid mixture with a suitable metal base. When this method of preparation is used, it is frequently possible to prepare a salt containing an excess of metal with respect to the number of equivalents of acid present; thus, mixed-acid metal salts containing as many as two equivalents and especially up to 1.5 equivalents of metal per equivalent of acid may be prepared. The equivalent of a metal for this purpose is its atomic weight divided by its valence.

Variants of the above-described methods may also be used to prepare the mixed-acid metal salts useful in this invention. For example, a metal salt of either acid may be blended with an acid of the other, and the resulting blend reacted with additional metal base.

Suitable metal bases for the preparation of the mixed-acid metal salts include the oxides, hydroxides, alkoxides and other basic salts of the metals previously enumerated, and in some cases the free metals themselves. Examples are sodium hydroxide, potassium hydroxide, magnesium oxide, calcium hydroxide, zinc oxide, lead oxide, nickel oxide and the like.

The temperature at which the mixed-acid metal salts are prepared is generally between 30°C and 150°C, preferably up to 125°C. If the mixed-acid salts are prepared by neutralization of a mixture of acids with a metal base, it is preferred to employ temperatures above 50°C and especially above 75°C. It is frequently advantageous to conduct the reaction in the presence of a substantially inert, normally liquid organic diluent such as naphtha, benzene, xylene, mineral oil and the like. If the diluent is mineral oil, it frequently need not be removed before using the mixed-acid metal salt as an additive for lubricants or functional fluids.

U. S. Patents 4,308,154 and 4,417,970 describe procedures for preparing these mixed-acid metal salts and disclose a number of examples of such mixed salts.

Type 2 - Metal hydrocarbyl dithiocarbamates.

The second type of oil-soluble metal salts used as component a) in the compositions of this invention are salts of one or more dithiocarbamic acids of the formula $RR'R''CSSH$ wherein R and R' are each independently hydrocarbyl groups in which the total number of carbon atoms in R and R' is sufficient to render the metal salt oil-soluble. R and R' taken together may represent a polymethylene or alkyl substituted polymethylene group thereby forming a cyclic com-

pound with the nitrogen atom (i.e., a monocyclic hydrocarbyl dithiocarbamate). Generally the hydrocarbyl groups will each contain at least two carbon atoms and may contain 50 or more carbon atoms. The metal component present in the dihydrocarbyl (or monocyclic hydrocarbyl) dithiocarbamate salts may be a monovalent metal or a polyvalent metal, although polyvalent metals are preferred as the salts of the polyvalent metals tend to possess better solubility in oils of lubricating viscosity. Thus although the alkali metal monocyclic hydrocarbyl or dihydrocarbyl dithiocarbamates may be used if oil-soluble, the preferred salts include, for example, salts of one or more of the alkaline earth metals, zinc, cadmium, magnesium, tin, molybdenum, iron, copper, nickel, cobalt, chromium, lead, etc. The Group II metal dihydrocarbyl dithiocarbamates are preferred.

In selecting a metal salt of a dithiocarbamic acid to be used in the compositions of this invention, R, R', and the metal may be varied so long as the metal salt is adequately oil-soluble. The nature and type of the mineral base stock, and the type of service contemplated for the treated lubricating oil should be taken into consideration in the choice of metal salt.

The metal constituent of the metal dihydrocarbyl dithiocarbamate is usually a simple metal cation. However in the case of certain polyvalent metal derivatives such as the tin and lead compounds, the metal constituent itself may be hydrocarbyl substituted (e.g., $(RR'_1N-CSS-)_xMR_1R_2$, where M is a polyvalent metal, R, R', R₁ and R₂ are, independently, hydrocarbyl groups (and, optionally R and R' taken together are a single cyclic hydrocarbyl group) in which the total number of carbon atoms is sufficient to render the compound oil-soluble, and x is an integer sufficient to satisfy the remaining valence(s) of M. Techniques described for example in U.S. Pat. No. 2,786,814 may be employed for preparing such hydrocarbyl-substituted metal dithiocarbamates.

Mixtures of metal salts of dithiocarbamic acids also are contemplated as being useful in the present invention. Such mixtures can be prepared by first preparing mixtures of dithiocarbamic acids and thereafter converting said acid mixtures to metal salts, or alternatively, metal salts of various dithiocarbamic acids can be prepared and thereafter mixed to give the desired product. Thus, the mixtures which can be incorporated in the compositions of the invention may be merely the physical mixture of the different metallic dithiocarbamic compounds, or compounds having different dithiocarbamate groupings attached to the same polyvalent metal atoms.

Examples of alkyl groups are ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, decyl, dodecyl, tridecyl, pentadecyl and hexadecyl groups including isomeric forms thereof. Examples of cycloalkyl groups include cyclohexyl and cycloheptyl groups, and examples of aralkyl groups include benzyl and phenethyl. Examples of polymethylene groups include penta- and hexamethylene groups, and examples of alkyl-substituted polymethylene groups include methyl pentamethylene, dimethyl pentamethylene, etc.

Specific examples of the metal dithiocarbamates useful as component a) in the compositions of this invention include zinc dibutyldithiocarbamate, zinc diamyldithiocarbamate, zinc di(2-ethylhexyl)dithiocarbamate, cadmium dibutyldithiocarbamate, cadmium dioctyldithiocarbamate, cadmium octylbutyldithiocarbamate, magnesium dibutyldithiocarbamate, magnesium dioctyldithiocarbamate, cadmium dicetyldithiocarbamate, copper diamyldithiocarbamate, sodium dioctadecyldithiocarbamate, lead dioctyldithiocarbamate, nickel diheptyldithiocarbamate, calcium di-2-ethylhexyldithiocarbamate, etc.

The various metal salts of dithiocarbamic acids utilized in the compositions of this invention are well known in the art and can be prepared by known techniques. See for example Ullmann, Encyklopadie der technischen Chemie, Band 10, Verlag Chemie, Weinheim, copyright 1975, pages 167-170 (and references cited therein); Thorn and Ludwig, The Dithiocarbamates and Related Compounds, Elsevier Publishing Company, 1962, pages 12 to 37 (and references cited therein); Delepine, Compt. Rend., 144, 1125 (1907); Whitby et al, Proceedings and Transactions of The Royal Society of Canada, XVIII, 111-114 (1924) (and references cited therein), Chabrier et al, Bulletin de la Societe Chimique De France, 1950, pages 43 et seq. (and references cited therein), and U. S. Pat. Nos. 1,622,534; 1,921,091; 2,046,875; 2,046,876; 2,258,847; 2,406,960; 2,443,160; 2,450,633; 2,492,314; 2,580,274; 3,513,094; 3,630,897; 4,178,258; and 4,226,733.

While boron is not a metallic element, boron tris(dihydrocarbyl dithiocarbamates) can be used as component a) of the compositions of this invention, either individually or in combination with one or more metal dihydrocarbyl dithiocarbamates. Methods suitable for the production of such boron dithiocarbamates are set forth in U.S. Pat. No. 4,879,071.

Derivatives of metal dihydrocarbyl dithiocarbamates may be used in addition to or in lieu of the metal dihydrocarbyl dithiocarbamates. Such derivatives include dithiocarbamate-derived phosphates such as are described in U.S. Pat. No. 4,919,830, reaction products of N,N-diorganodithiocarbamates with thionyl chloride such as are described in U.S. Pat. No. 4,867,893, N,N-diorganodithiocarbamate-alkylthiosulfinyl halide reaction products such as are described in U.S. Pat. No. 4,859,356, reaction products of halogenated EPDM terpolymers and alkali metal dialkyldithiocarbamate such as are described in U.S. Pat. No. 4,502,972, and sulfurized metal dihydrocarbyl dithiocarbamates such as are described in U.S. Pat. No. 4,360,438, among others. In addition, the metal dihydrocarbyl dithiocarbamates may be used in combination with other carbamate compounds such as for example, a 1,2-dicarbethoxyethyl dialkyldithiocarbamate such as is disclosed in U.S. Pat. No. 4,479,883; or a mercaptoalkanoic acid dithiocarbamate of the type described in U.S. Pat. No. 3,890,363. Mixtures of different metal dihydrocarbyl dithiocarbamates as well as combinations of (1) one or more

metal dihydrocarbyl dithiophosphates and (2) one or more metal dihydrocarbyl dithiocarbamates can be used as component a) in the practice of this invention.

Component b)

The ashless dispersant which is used in the process is preferably a preformed ashless dispersant as described above containing basic nitrogen. Thus, for example, any suitable boron-free ashless dispersant formed in the customary manner can be heated with phosphorous acid to cause phosphorylation to occur. The resulting liquid product composition when subjected to chemical analysis reveals the presence of phosphorus.

Rather than utilizing a preformed ashless dispersant containing basic nitrogen, it is possible to produce component b) by:

- 1) forming the ashless dispersant in the presence of phosphorous acid; or
- 2) heating phosphorous acid with a basic nitrogen-containing reactant used in forming the ashless dispersant, and using the resultant phosphorylated reactant to form the ashless dispersant.

In all such cases, the final product composition [component b)] should be a liquid that on analysis reveals the presence of phosphorus. Such product composition should also exhibit dispersant properties. In any case wherein an ashless dispersant used in forming component b) is not a liquid but rather is in whole or in part in the solid state of aggregation at room temperature (e.g., 25°C), it is preferable to dissolve such dispersant in a suitable solvent or diluent (polar or non-polar, as may be required to dissolve the dispersant) before the dispersant is subjected to phosphorylation in forming component b). In this connection, the phrase "such that a liquid boron-free phosphorus-containing composition is formed" as used herein in connection with such solid state dispersants means that component b), including such solvent or diluent, is in the liquid state of aggregation at room temperature (e.g., 25°C), even though at a lower temperature the dispersant may revert in whole or in part to the solid state. Of course in any case, component b) must be oil-soluble within the meaning of such term as set forth hereinafter.

Irrespective of the method used in forming component b), in any instance wherein macro (i.e., non-dispersible) solids are formed or remain in the liquid composition after it has been formed, such solids should be removed, and can be readily removed, by any of a variety of conventional separation techniques such as filtration, centrifugation, decantation, or the like.

The actual chemical structures of the final product compositions used as component b) in the practice of this invention, however prepared, are not known with absolute certainty. While it is believed that phosphorus-containing moieties are chemically bonded to the ashless dispersant, it is possible that component b) is in whole or in part a micellar structure containing phosphorus-containing species or moieties. Thus, this invention is not limited to, and should not be construed as being limited to, any specific structural configurations with respect to component b). As noted above, all that is required is that component b) is a liquid that is oil soluble and that if subjected to analysis reveals the presence of phosphorus. In addition, component b) should possess dispersant properties.

Although any of a variety of standard methods can be used to analyze the phosphorylated dispersant for the presence of phosphorus therein, it is desirable to use the analytical procedure set forth in ASTM D-4951. In this procedure it is convenient to use a Perkin-Elmer Plasma 40 Emission Spectrometer. The analyzing wavelength for acceptable measurements for phosphorus is 213.618 nm.

It is to be understood and appreciated that component b) may contain chemical species and/or moieties besides the phosphorus-containing species or moieties such as, for example, nitrogen- and/or oxygen- and/or sulfur-containing species or moieties over and above the basic nitrogen and/or hydroxyl group(s) forming an essential part of the initial ashless dispersant itself. The only qualification to the foregoing is that component b) is itself boron-free. It is also to be understood and appreciated that organic phosphorus-containing compounds may be used along with phosphorous acid in making component b). Further, the phosphorous acid can be formed in situ, as, for example, by heating a mixture of an inorganic phosphorus oxide and water.

As used herein, the term "phosphorylated" means that the ashless dispersant has been heated with phosphorous acid such that the resultant product, on analysis, reveals the presence of phosphorus. As noted hereinabove, the precise chemical makeup of the phosphorylated dispersant compositions is not known with absolute certainty. Thus the term "phosphorylated" is not to be construed as requiring that the resultant composition contain chemically bound phosphorus. While it is believed that chemical reactions do occur to produce a composition containing at least some chemically bound phosphorus moieties, moieties or species of phosphorus conceivably could be present, at least in part, in the form of micellar structures.

The dispersant used in the formation of component b) is a polyamine succinimide in which the succinic group contains an acyclic hydrocarbyl substituent typically containing at least 30 carbon atoms. The polyamine used in forming such compounds is a mixture of ethylene polyamine as described above and contains at least one primary amino group

capable of forming an imide group on reaction with a hydrocarbon-substituted succinic acid or acid derivative thereof such as anhydride lower alkyl ester, acid halide, or acid-ester. Mixtures generally corresponding in overall makeup to tetraethylene pentamine are most preferred.

The alkenyl succinimides may be formed by conventional methods such as by heating an alkenyl succinic anhydride, acid, acid-ester, acid halide, or lower alkyl ester with a polyamine containing at least one primary amino group. The alkenyl succinic anhydride may be made readily by heating a mixture of olefin and maleic anhydride to 180°-220°C. The olefin is preferably a polymer or copolymer of a lower monolefin such as ethylene, propylene, 1-butene, isobutene and the like. The more preferred source of alkenyl group is from polyisobutene having a number average molecular weight of up to 100,000 or higher. In a still more preferred embodiment the alkenyl group is a polyisobutenyl group having a number average molecular weight (determined using the method described in detail hereinafter) of 500-5,000, and preferably 700-2,500, more preferably 700-1,400, and especially 800-1,200. The isobutene used in making the polyisobutene is usually (but not necessarily) a mixture of isobutene and other C₄ isomers such as 1-butene. Thus, strictly speaking, the acylating agent formed from maleic anhydride and "polyisobutene" made from such mixtures of isobutene and other C₄ isomers such as 1-butene, can be termed a "polybutenyl succinic anhydride" and a succinimide made therewith can be termed a "polybutenyl succinimide". However, it is common to refer to such substances as "polyisobutenyl succinic anhydride" and "polyisobutenyl succinimide", respectively. As used herein "polyisobutenyl" is used to denote the alkenyl moiety whether made from a highly pure isobutene or a more impure mixture of isobutene and other C₄ isomers such as 1-butene.

Especially preferred ashless dispersants for use in the present invention are the products of reaction of a polyethylene polyamine, e.g. triethylene tetramine or tetraethylene pentamine, with a hydrocarbon-substituted carboxylic acid or anhydride (or other suitable acid derivative) made by reaction of a polyolefin, preferably polyisobutene, having a number average molecular weight of 500 to 5,000, preferably 700 to 2,500, more preferably 700 to 1,400 and especially 800 to 1,200, with an unsaturated polycarboxylic acid or anhydride, e.g., maleic anhydride, maleic acid, fumaric acid, or the like, including mixtures of two or more such substances.

As used herein the term "succinimide" is meant to encompass the completed reaction product from reaction between the amine reactant(s) and the hydrocarbon-substituted carboxylic acid or anhydride (or like acid derivative) reactant(s), and is intended to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

Residual unsaturation in the alkenyl group of the alkenyl succinimide may be used as a reaction site, if desired. For example the alkenyl substituent may be hydrogenated, hydrohalogenated or the like. Ordinarily, there is little to be gained by use of such techniques, and thus the use of alkenyl succinimides as the precursor of component b) is preferred.

It is also possible after using the phosphorylation procedures described herein to post-treat the phosphorylated ashless dispersant using any prior art-type post-treating procedure (except boronation), again provided that the resultant post-treated ashless dispersant is boron-free and contains at least some residual basic nitrogen.

Because of environmental and conservational concerns it is desirable to employ ashless dispersants which contain little, if any, halogen atoms such as chlorine atoms. Thus, in order to satisfy such concerns, it is desirable (although in many cases not necessary from a performance standpoint) to select ashless dispersants (as well as the other components used in the compositions of this invention) such that the total halogen content, if any, of the overall lubricant or functional fluid composition does not exceed 100 ppm. Indeed, the lower the better. Likewise, it is preferable in accordance with this invention, to provide additive concentrates which, when dissolved in a halogen-free base oil, at a concentration of 10% by weight, yield an oleaginous composition in which the total halogen content, if any, is 100 ppm or less.

Typical procedures for producing the phosphorylated ashless dispersants involve heating one or more ashless dispersants of the type described above with phosphorous acid (H₃PO₃, sometimes depicted as H₂(HPO₃), and sometimes called ortho-phosphorous acid), under conditions yielding a liquid phosphorous-containing composition.

Optionally, additional sources of basic nitrogen can be included in the phosphorous acid ashless dispersant mixture so as to provide a molar amount (atomic proportion) of basic nitrogen up to that equal to the molar amount of basic nitrogen contributed by the ashless dispersant. Preferred auxiliary nitrogen compounds are long chain primary, secondary and tertiary alkyl amines containing from 12 to 24 carbon atoms, including their hydroxyalkyl and aminoalkyl derivatives. The long chain alkyl group may optionally contain one or more ether groups. Examples of suitable compounds are oleyl amine, N-oleyltrimethylene diamine, N-tallow diethanolamine, N,N-dimethyl oleylamine, and myristyloxapropyl amine.

Other materials normally used in lubricant additives which do not interfere with the process may also be added, for example, a benzotriazole, including lower (C₁-C₄) alkyl-substituted benzotriazoles, which function to protect copper surfaces.

The heating step is conducted at temperatures sufficient to produce a liquid composition which contains phosphorous. The heating can be carried out in the absence of a solvent by heating a mixture of the ashless dispersant and phosphorous acid. The temperatures used will vary somewhat depending upon the nature of the ashless dispersant

being utilized. Generally speaking however, the temperature will usually fall within the range of 40 to 200°C. The duration of the heating is likewise susceptible to variation, but ordinarily will fall in the range of 1 to 3 hours. When conducting the heating in bulk, it is important to thoroughly agitate the components to ensure intimate contact therebetween. When utilizing solid phosphorous acid, it is convenient to apply heat to the mixture until a clear liquid composition is formed. Alternatively, the phosphorous acid may be utilized in the form of an aqueous solution. Water formed in the process and any added water is preferably removed from the heated mixture by vacuum distillation at temperatures of from 100 to 140°C. The heating may be conducted in more than one stage if desired. Preferably the heating step or steps will be conducted in a diluent oil or other inert liquid medium such as light mineral oils.

The amount of phosphorous acid employed in the heating process preferably ranges from 0.001 mole to 0.999 mole per mole of basic nitrogen and free hydroxyl in the mixture being heated, up to one half of which may be contributed by an auxiliary nitrogen compound. It is possible however to use the phosphorous acid in excess of the amount of basic nitrogen and/or hydroxyl groups in the dispersant being heated.

When used, the amount of diluent usually ranges from 10 to 50% by weight of the mixture being subjected to heating. Water can be added to the mixture, before and/or during the heating, if desired.

Usually the phosphorylated dispersants utilized as component b) in the compositions of this invention when in their undiluted state will have on a weight basis a phosphorus content of at least 5,000 parts per million (ppm) (preferably at least 6,000 ppm and more preferably at least 7,000 ppm). When forming component b) the phosphorous acid should be used in an amount sufficient to provide at least 25% (preferably at least 50% and more preferably at least 75%) of the total content of phosphorous in the phosphorylated dispersant.

The preparation of phosphorylated ashless dispersants suitable for use as component b) in the compositions of this invention is illustrated by the following examples in which all parts and percentages are by weight unless otherwise clearly specified.

EXAMPLE B-1

A mixture is formed from 260 parts of a polyisobutenyl succinimide ashless dispersant (derived from polybutene having a number average molecular weight of about 950 and a mixture of a polyethylene polyamines having an average overall composition approximating that of tetraethylene pentamine), 100 parts of a 100 Solvent Neutral refined mineral oil diluent, 8 parts of solid phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 110°C for two hours. A vacuum of 40 mm Hg is gradually drawn on the product to remove traces of water while the temperature is maintained at 110°C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

EXAMPLE B-2

The procedure of Example B-1 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 1,150. The average number of succinic groups per alkenyl group in the succinimide is approximately 1.2.

EXAMPLE B-3

The procedure of Example B-1 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 2,100.

EXAMPLE B-4

The procedures of Examples B-1 through B-3 are repeated except that the tolutriazole is omitted from the initial mixtures subjected to the thermal processes.

EXAMPLE B-5

To 2,500 parts of a polyisobutenyl succinimide (derived from polyisobutene having a number average molecular weight of 950 and a mixture of polyethylene polyamines having an overall average composition approximating that of tetraethylene pentamine) warmed to 28°C are added 54.31 parts of phosphorous acid, 20.27 parts of tolutriazole and 23.91 parts of water. This mixture is heated at 110°C for 1.5 hours. Then the reflux condenser is replaced by a distillation column and water is removed under vacuum for 2.25 hours at 110°C to form a homogeneous liquid composition suitable for use as component b) in the practice of this invention.

EXAMPLE B-6

A mixture of 7300 parts of a polyisobutenyl succinimide (derived from polybutene having a number average molecular weight of about 1,300 and a mixture of polyethylene polyamines having an average overall composition approximating that of tetraethylene pentamine), and 2500 parts of 100 Solvent Neutral mineral oil is heated to 90-100°C. To this mixture is added 200 parts of phosphorous acid and the resultant mixture is heated at 90-100°C for 2 hours. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

EXAMPLE B-7

A mixture of 58,415.5 parts of a polyisobutenyl succinimide (derived from polyisobutene having a number average molecular weight of 1300 and a mixture of polyethylene polyamines having an overall average composition approximating that of tetraethylene pentamine), and 12,661.6 parts of 100 Solvent Neutral mineral oil is heated to 80°C. To this mixture is added 1942.28 parts of phosphorous acid and the resultant mixture is heated at 110°C for 2 hours. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

EXAMPLE B-8

The procedure of Example B-7 is repeated using 45,600 parts of the ashless dispersant, 8983.2 parts of the mineral oil diluent, and 2416.8 parts of the phosphorous acid.

EXAMPLE B-9

A mixture of 14,400 parts of a polyisobutenyl succinimide (derived from polyisobutene having a number average molecular weight of 950 and a mixture of polyethylene polyamines having an overall average composition approximating that of tetraethylene pentamine), and 3121.2 parts of 100 Solvent Neutral mineral oil is heated to 80°C. To this mixture is added 478.8 parts of phosphorous acid and the resultant mixture is heated at 110°C for 2 hours. The resultant homogeneous liquid composition contains about 1.04% of phosphorus and is suitable for use as component b) in the practice of this invention.

EXAMPLE B-10

A mixture of 7300 parts of ashless dispersant as used in Example B-6 2500 parts of 100 Solvent Neutral mineral oil, and 200 parts of phosphorous acid is formed at room temperature and heated to 110°C for two hours. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

EXAMPLE B-11

A mixture of 4680 parts of phosphorylated dispersant formed as in Example B-10 and 2340 parts of a commercial boronated succinimide ashless dispersant (HITEC® 648 dispersant; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.) is formed. The resultant homogeneous liquid composition is suitable for use in the practice of this invention. A portion of the resultant mixture can be heated to 110°C for two hours, and this resultant homogeneous liquid composition is also suitable for use as component b) in the practice of this invention.

EXAMPLE B-12

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($M_n = 2020$; $M_w = 6049$, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 57 parts (1.38 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 1,067 parts of mineral oil and 893 parts (1.38 equivalents) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140-145°C. The reaction mixture is then heated to 155°C over a three hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominately of polyisobutenyl succinimides.

(c) A mixture is formed from 250 parts of the polyisobutenyl succinimide product solution formed as in (b), 8 parts of phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 100°C for two hours. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

EXAMPLE B-13

The procedure of Example B-12 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE B-14

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ($M_n = 2020$; $M_w = 6049$, both determined using the methodology of U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110°C. This mixture is heated to 184°C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189°C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190°C with nitrogen purged for 26 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 18.2 parts (0.433 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 392 parts of mineral oil and 348 parts (0.52 equivalent) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140°C. The reaction mixture is then heated to 150°C in 1.8 hours and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominately of polyisobutenyl succinimides.

(c) A mixture is formed from 250 parts of the polyisobutenyl succinimide product solution formed as in (b), 8 parts of phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 100°C for two hours. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

EXAMPLE B-15

The procedure of Example B-14 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE B-16

(a) A mixture of 510 parts (0.28 mole) of polyisobutene ($M_n = 1845$; $M_w = 5325$, both determined using the methodology of U.S. Pat. No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110°C. This mixture is heated to 190°C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192°C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193°C with nitrogen blowing for 10 hours. The residue is predominately polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 10.2 parts (0.25 equivalent) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 113 parts of mineral oil and 161 parts (0.25 equivalent) of the substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 138°C. The reaction mixture is heated to 150°C over a 2 hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 125 parts of the polyisobutenyl succinimide product solution formed as in (b), 8 parts of phosphorous acid, and 3.5 parts of tolutriazole. The mixture is heated at 100°C. to form a composition which is soluble in oil and suitable for use as component b).

EXAMPLE B-17

The procedure of Example B-16 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

EXAMPLE 18

To a reactor are charged under a nitrogen atmosphere 67.98 parts of a commercially-available polyisobutenyl succinimide of a mixture of polyethylene polyamines having the approximate overall composition of tetraethylene pentamine (the polyisobutenyl group derived from polyisobutene having a number average molecular weight of about 950; the succinimide product having a ratio of about 1.15 succinic groups per alkenyl group) and 26.14 parts of a 100 Solvent Neutral refined mineral oil. After raising the temperature of the resulting solution to 100-105°C, 2.09 parts of phosphorous

acid are introduced into the reactor, followed by 0.92 part of toluotriazole (Cobratec TT-100; PMC Specialties Group, Cincinnati, Ohio). The resultant mixture is heated at 100-105°C for two hours. Then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component b) in the compositions of this invention.

EXAMPLE 19

The procedure of Example B-18 is repeated except that the toluotriazole is omitted from the reaction mixture.

EXAMPLE 20

The procedure of Example B-19 is repeated except that 763.2 parts of phosphorous acid (H_3PO_3) and 2,836.8 parts of 100 Solvent Neutral mineral oil are used. The phosphorus content of the final product is about 1.66%.

EXAMPLE B-21

(a) To 120 parts of chlorinated polyisobutylene having a number average molecular weight of about 1,300 and containing about 2.8 weight percent chlorine are added 21.7 parts of pentaethylene hexamine and 5.6 parts of sodium carbonate. The reaction mixture is heated to about 205°C and maintained at this temperature for about 5 hours. A stream of nitrogen is passed through the reaction mixture to remove the water of reaction. The reaction mixture is diluted with 60 parts of light mineral oil and hexane, filtered and extracted with methanol to remove excess pentaethylene hexamine. The hexane is stripped from the product by heating the mixture to 120°C under a suitable vacuum. The product should have a nitrogen content of approximately 1.0 to 1.5 weight percent.

(b) A mixture is formed from 80 parts of a diluted reaction product formed as in (a), 20 parts of a 100 Solvent Neutral refined mineral oil diluent, and 2.1 parts of phosphorous acid. The resultant mixture is heated at 100-105°C for 2 hours and then the temperature is gradually raised to 115°C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120°C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component b) in the compositions of this invention.

EXAMPLE B-22

The procedure of Example B-9 is repeated except that the proportions of the reaction components are 14,400 parts of the succinimide, 3409.2 parts of the mineral oil, and 190.8 parts of phosphorous acid (H_3PO_3). This product contains approximately 0.40% of phosphorous.

EXAMPLE B-23

The procedure of Example B-7 is repeated except that the proportions of the reaction components are 45,600 parts of the succinimide, 10,795.8 parts of the process oil, and 604.2 parts of phosphorous acid (H_3PO_3). This product contains approximately 0.41% of phosphorous.

A particularly preferred embodiment of this invention involves using as component b) a phosphorylated alkenyl succinimide as described wherein the succinimide is formed from (i) an alkenyl succinic acylating agent having a succination ratio (i.e., the ratio of the average number of chemically bound succinic groups per alkenyl group in the molecular structure of the succinic acylating agent) in the range of 1 to about 1.3, the alkenyl group being derived from a polyolefin (most preferably a polyisobutene) having a number of average molecular weight in the range of about 600 to about 1,300 (more preferably in the range of 700 to 1,250 and most preferably in the range of 800 to 1,200).

The number average molecular weight (\bar{M}_n) of the polyalkene from which the substituent is derived is determined by use of either of two methods, namely, vapor pressure osmometry (VPO) or gel permeation chromatography (GPC). VPO determination should be conducted in accordance with ASTM D-2503-82 using high purity toluene as the measuring solvent. Alternatively, a GPC procedure can be employed. As is well known, the GPC technique involves separating molecules according to their size in solution. For this purpose liquid chromatographic columns are packed with a styrenedivinyl benzene copolymer of controlled particle and pore sizes. When the polyalkene molecules from which the substituent is derived are transported through the GPC columns by a solvent (tetrahydrofuran), the polyalkene molecules small enough to penetrate into the pores of the column packing are retarded in their progress through the columns. On the other hand, the polyalkene molecules which are larger either penetrate the pores only slightly or are totally excluded from the pores. As a consequence, these larger polyalkene molecules are retarded in their progress through the columns

to a lesser extent. Thus a velocity separation occurs according to the size of the respective polyalkene molecules. In order to define the relationship between polyalkene molecular weight and elution time, the GPC system to be used is calibrated using known molecular weight polyalkene standards and an internal standard method. Details concerning such GPC procedures and methods for column calibration are extensively reported in the literature. See for example, W. W. Yau, J. J. Kirkland, and D. D. Bly, Modern Size-Exclusion Liquid Chromatography, John Wiley & Sons, 1979, Chapter 9 (pages 285-341), and references cited therein.

Component c)

The metal-containing detergents which preferably are employed in conjunction with components a) and b) of the compositions of this invention are exemplified by oil-soluble basic salts of alkali or alkaline earth metals with one or more of the following acidic substances (or mixtures thereof): (1) sulfonic acids, (2) carboxylic acids, (3) salicylic acids, (4) alkylphenols, (5) sulfurized alkylphenols, (6) organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage. Such organic phosphorus acids include those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1,000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium. The detergents for use as component c) are typically basic salts having a TBN of at least 50, preferably above 200, more preferably above 250, and still more preferably 300 or above.

The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature of about 50°C, and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve alcohol, Carbitol alcohol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, phenyl-beta-naphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent and at least one alcohol promoter, and carbonating the mixture at an elevated temperature such as 60°-200°C.

Examples of suitable metal-containing detergents include, but are not limited to, the basic or overbased salts of such substances as lithium phenates, sodium phenates, potassium phenates, calcium phenates, magnesium phenates, sulfurized lithium phenates, sulfurized sodium phenates, sulfurized potassium phenates, sulfurized calcium phenates, and sulfurized magnesium phenates wherein each aromatic group has one or more aliphatic groups to impart hydrocarbon solubility; lithium sulfonates, sodium sulfonates, potassium sulfonates, calcium sulfonates, and magnesium sulfonates wherein each sulfonic acid moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility; lithium salicylates, sodium salicylates, potassium salicylates, calcium salicylates, and magnesium salicylates wherein the aromatic moiety is usually substituted by one or more aliphatic substituents to impart hydrocarbon solubility; the lithium, sodium, potassium, calcium and magnesium salts of hydrolyzed phosphosulfurized olefins having 10 to 2000 carbon atoms or of hydrolyzed phosphosulfurized alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2000 carbon atoms; lithium, sodium, potassium, calcium and magnesium salts of aliphatic carboxylic acids and aliphatic-substituted cycloaliphatic carboxylic acids; and many other similar alkali and alkaline earth metal salts of oil-soluble organic acids. Mixtures of basic or overbased salts of two or more different alkali and/or alkaline earth metals can be used. Likewise, basic or overbased salts of mixtures of two or more different acids or two or more different types of acids (e.g., one or more calcium phenates with one or more calcium sulfonates) can also be used. While rubidium, cesium and strontium salts are feasible, their expense renders them impractical for most uses. Likewise, while barium salts are effective, the status of barium as a heavy metal under a toxicological cloud renders barium salts less preferred for present-day usage.

As is well known, overbased metal detergents are generally regarded as containing overbasing quantities of inorganic bases, probably in the form of micro dispersions or colloidal suspensions. Thus the term "oil-soluble" as applied to component c) materials is intended to include metal detergents wherein inorganic bases are present that are not necessarily completely or truly oil-soluble in the strict sense of the term, inasmuch as such detergents when mixed into base oils behave in much the same way as if they were fully and totally dissolved in the oil.

Collectively, the various basic or overbased detergents referred to hereinabove, have sometimes been called, quite simply, basic alkali metal or alkaline earth metal-containing organic acid salts.

Methods for the production of oil-soluble basic and overbased alkali and alkaline earth metal-containing detergents are well known to those skilled in the art and are extensively reported in the patent literature. See for example, U.S. Pat.

Nos. 2,451,345; 2,451,346; 2,485,861; 2,501,731; 2,501,732; 2,585,520; 2,671,758; 2,616,904; 2,616,905; 2,616,906; 2,616,911; 2,616,924; 2,616,925; 2,617,049; 2,695,910; 3,178,368; 3,367,867; 3,496,105; 3,629,109; 3,865,737; 3,907,691; 4,100,085; 4,129,589; 4,137,184; 4,148,740; 4,212,752; 4,617,135; 4,647,387; 4,880,550; GB Published Patent Application 2,082,619 A, and European Patent Application Publication Nos. 121,024 B1 and 259,974 A2.

The basic or overbased metal detergents utilized as component c) can, if desired, be oil-soluble boronated alkali or alkaline earth metal-containing detergents. Methods for preparing boronated, overbased metal detergents are described, for example, in U.S. Pat. Nos. 3,480,548; 3,679,584; 3,829,381; 3,909,691; 4,965,003; and 4,965,004.

Particularly preferred metal detergents for use as component c) are one or more calcium sulfonates, one or more magnesium sulfonates, or combinations of one or more calcium sulfonates and one or more magnesium sulfonates, and

Most preferred are one or more overbased calcium sulfonates, one or more overbased magnesium sulfonates, and combinations of one or more overbased calcium sulfonates and one or more overbased magnesium sulfonates.

Component d)

As noted above, in situations where scuffing wear is likely to be encountered, it is desirable to combine one or more boron-containing additive components with components a) and b) or with components a), b), and c). The boron-containing additive components are preferably oil-soluble additive components, but effective use can be made of boron-containing components which are sufficiently finely divided as to form stable dispersions in the base oil. Examples of the latter type of boron-containing components include the finely-divided inorganic orthoborate salts such as lithium borate, sodium borate, potassium borate, magnesium borate, calcium borate, ammonium borate and the like.

The oil-soluble boron-containing components include boronated ashless dispersants (often referred to as borated ashless dispersants) and esters of acids of boron. Examples of boronated ashless dispersants and descriptions of methods by which they can be prepared are well-documented in the literature. See for example U.S. Pat. Nos. 3,087,936; 3,254,025; 3,281,428; 3,282,955; 3,533,945; 3,539,633; 3,658,836; 3,697,574; 3,703,536; 3,704,308; 4,025,445; and 4,857,214. Likewise the literature is replete with examples of oil-soluble esters of boron acids and methods for their production. See for example the disclosures of U.S. Pat. Nos. 2,866,811; 2,931,774; 3,009,797; 3,009,798; 3,009,799; 3,014,061; and 3,092,586.

Other Additive Components

The lubricant and lubricant concentrates of this invention can and preferably will contain additional components in order to partake of the properties which can be conferred to the overall composition by such additional components. The nature of such components will, to a large extent, be governed by the particular use to which the ultimate oleaginous composition (lubricant or functional fluid) is to be subjected.

Antioxidants.

Most oleaginous compositions will contain a conventional quantity of one or more antioxidants in order to protect the composition from premature degradation in the presence of air, especially at elevated temperatures. Typical antioxidants include hindered phenolic antioxidants, secondary aromatic amine antioxidants, sulfurized phenolic antioxidants, oil-soluble copper compounds, phosphorus-containing antioxidants, and the like.

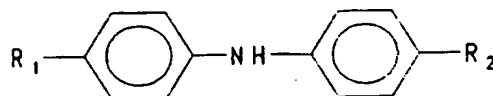
Illustrative sterically hindered phenolic antioxidants include ortho-alkylated phenolic compounds such as 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 2-tert-butylphenol, 2,6-diisopropylphenol, 2-methyl-6-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol, 4-(N,N-dimethylaminomethyl)-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 2-methyl-6-styrylphenol, 2,6-di-styryl-4-nonylphenol, and their analogs and homologs. Mixtures of two or more such mononuclear phenolic compounds are also suitable.

The preferred antioxidants for use in the compositions of this invention are methylene-bridged alkylphenols, and these can be used singly or in combinations with each other, or in combinations with sterically-hindered unbridged phenolic compounds. Illustrative methylene bridged compounds include 4,4'-methylenebis(6-tert-butyl-o-cresol), 4,4'-methylenebis(2-tert-amyl-o-cresol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-methylenebis(2,6-di-tert-butylphenol), and similar compounds. Particularly preferred are mixtures of methylene-bridged alkylphenols such as are described in U.S. Pat. No. 3,211,652.

Amine antioxidants, especially oil-soluble aromatic secondary amines can also be used in the compositions of this invention. Whilst aromatic secondary monoamines are preferred, aromatic secondary polyamines are also suitable. Illustrative aromatic secondary monoamines include diphenylamine, alkyl diphenylamines containing 1 or 2 alkyl substituents each having up to 16 carbon atoms, phenyl- α -naphthylamine, phenyl- β -naphthylamine, alkyl- or aralkyl-substituted phenyl- α -naphthylamine containing one or two alkyl or aralkyl groups each having up to 16 carbon atoms, alkyl- or aralkyl-substituted phenyl- β -naphthylamine containing one or two alkyl or aralkyl groups each having up to 16 carbon

atoms, and similar compounds.

A preferred type of aromatic amine antioxidant is an alkylated diphenylamine of the general formula



wherein R_1 is an alkyl group (preferably a branched alkyl group) having 8 to 12 carbon atoms, (more preferably 8 or 9 carbon atoms) and R_2 is a hydrogen atom or an alkyl group (preferably a branched alkyl group) having 8 to 12 carbon atoms, (more preferably 8 or 9 carbon atoms). Most preferably, R_1 and R_2 are the same. One such preferred compound is available commercially as Naugalube 438L, a material which is understood to be predominately a 4,4'-dinonyldiphenylamine (i.e., bis(4-nonylphenyl)amine) wherein the nonyl groups are branched.

Another useful type of antioxidant for inclusion in the compositions of this invention is comprised to one or more liquid, partially sulfurized phenolic compounds such as are prepared by reacting sulfur monochloride with a liquid mixture of phenols -- at least 50 weight percent of which mixture of phenols is composed of one or more reactive, hindered phenols -- in proportions to provide from 0.3 to 0.7 gram atoms of sulfur monochloride per mole of reactive, hindered phenol so as to produce a liquid product. Typical phenol mixtures useful in making such liquid product compositions include a mixture containing by weight about 75% of 2,6-di-tert-butylphenol, about 10% of 2-tert-butylphenol, about 13% of 2,4,6-tri-tert-butylphenol, and about 2% of 2,4-di-tert-butylphenol. The reaction is exothermic and thus is preferably kept within the range of 15°C to 70°C, most preferably between 40°C to 60°C.

Mixtures of different antioxidants can also be used. One suitable mixture is comprised of a combination of (i) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated monohydric phenols which is in the liquid state at 25°C, (ii) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated methylene-bridged polyphenols, and (iii) at least one bis(4-alkylphenyl)amine wherein the alkyl group is a branched alkyl group having 8 to 12 carbon atoms, the proportions of (i), (ii) and (iii) on a weight basis falling in the range of 3.5 to 5.0 parts of component (i) and 0.9 to 1.2 parts of component (ii) per part by weight of component (iii).

The lubricating compositions of this invention preferably contain 0.01 to 1.0% by weight, more preferably 0.05 to 0.7% by weight, of one or more sterically-hindered phenolic antioxidants of the types described above. Alternatively or additionally the lubricants of this invention may contain 0.01 to 1.0% by weight, more preferably 0.05 to 0.7% by weight of one or more aromatic amine antioxidants of the types described above.

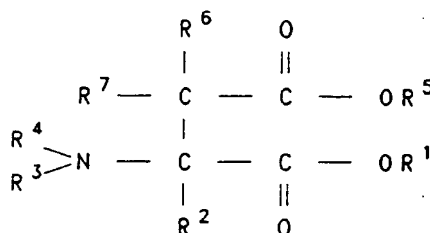
Corrosion Inhibitors.

It is also preferred pursuant to this invention to employ in the lubricant compositions and additive concentrates a suitable quantity of a corrosion inhibitor. This may be a single compound or a mixture of compounds having the property of inhibiting corrosion of metallic surfaces.

One type of such additives are inhibitors of copper corrosion. Such compounds include thiazoles, triazoles and thiadiazoles. Examples of such compounds include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles, 2,5-bis(hydrocarbylthio)-1,3,4-thiadiazoles, and 2,5-(bis)hydrocarbyldithio-1,3,4-thiadiazoles. The preferred compounds are the 1,3,4-thiadiazoles, a number of which are available as articles of commerce. For synthesis procedures, see for example U.S. Pat. Nos. 2,765,289; 2,749,311; 2,760,933; 2,850,453; 2,910,439; 3,663,561; 3,862,798; and 3,840,549.

Other types of corrosion inhibitors suitable for use in the compositions of this invention include dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, linoleic acid, or the like. Products of this type are currently available from various, commercial sources, such as, for example, the dimer and trimer acids sold under the HYSTRENE trademark by the Humco Chemical Division of Witco Chemical Corporation and under the EMPOL trademark by Emery Chemicals. Another useful type of corrosion inhibitor for use in the practice of this invention are the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, and the like. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Other suitable corrosion inhibitors include ether amines; acid phosphates; amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; and the like. Materials of these types are well known to those skilled in the art and a number of such materials are available as articles of commerce.

Other useful corrosion inhibitors are aminosuccinic acids or derivatives thereof represented by the formula:



wherein each of R¹, R², R⁵, R⁶ and R⁷ is, independently, a hydrogen atom or a hydrocarbonyl group containing 1 to 30 carbon atoms, and wherein each of R³ and R⁴ is, independently, a hydrogen atom, a hydrocarbonyl group containing 1 to 30 carbon atoms, or an acyl group containing from 1 to 30 carbon atoms. The groups R¹, R², R³, R⁴, R⁵, R⁶ and R⁷, when in the form of hydrocarbonyl groups, can be, for example, alkyl, cycloalkyl or aromatic containing groups. Preferably R¹ and R⁵ are the same or different straight-chain or branched-chain hydrocarbon radicals containing 1-20 carbon atoms. Most preferably, R¹ and R⁵ are saturated hydrocarbon radicals containing 3-6 carbon atoms. R², either R³ or R⁴, R⁶ and R⁷, when in the form of hydrocarbonyl groups, are preferably the same or different straight-chain or branched-chain saturated hydrocarbon radicals. Preferably a dialkyl ester of an aminosuccinic acid is used in which R¹ and R⁵ are the same or different alkyl groups containing 3-6 carbon atoms, R² is a hydrogen atom, and either R³ or R⁴ is an alkyl group containing 15-20 carbon atoms or an acyl group which is derived from a saturated or unsaturated carboxylic acid containing 2-10 carbon atoms.

Most preferred of the aminosuccinic acid derivatives is a dialkylester of an aminosuccinic acid of the above formula wherein R¹ and R⁵ are isobutyl, R² is a hydrogen atom, R³ is octadecyl and/or octadecenyl and R⁴ is 3-carboxy-1-oxo-2-propenyl. In such ester R⁶ and R⁷ are most preferably hydrogen atoms.

The lubricant compositions of this invention most preferably contain from 0.005 to 0.5% by weight, and especially from 0.01 to 0.2% by weight, of one or more corrosion inhibitors and/or metal deactivators of the type described above.

Antifoam Agents.

Suitable antifoam agents include silicones and organic polymers such as acrylate polymers. Various antifoam agents are described in Foam Control Agents by H. T. Kerner (Noyes Data Corporation, 1976, pages 125-176). Mixtures of silicone-type antifoam agents such as the liquid dialkyl silicone polymers with various other substances are also effective. Typical of such mixtures are silicones mixed with an acrylate polymer, silicones mixed with one or more amines, and silicones mixed with one or more amine carboxylates.

Neutral Metal-Containing Detergents.

For some applications such as crankcase lubricants for diesel engines, it is desirable to include an oil-soluble neutral metal-containing detergent in which the metal is an alkali metal or an alkaline earth metal. Combinations of such detergents can also be employed. The neutral detergents of this type are those which contain an essentially stoichiometric equivalent quantity of metal in relation to the amount of acidic moieties present in the detergent. Thus in general, the neutral detergents will have a TBN of up to about 50.

The acidic materials utilized in forming such detergents include carboxylic acids, salicylic acids, alkylphenols, sulfonic acids, sulfurized alkylphenols, and the like. Typical detergents of this type and/or methods for their preparation are known and reported in the literature. See for example U.S. Pat. Nos. 2,001,108; 2,081,075; 2,095,538; 2,144,078; 2,163,622; 2,180,697; 2,180,698; 2,180,699; 2,211,972; 2,223,127; 2,228,654; 2,228,661; 2,249,626; 2,252,793; 2,270,183; 2,281,824; 2,289,795; 2,292,205; 2,294,145; 2,321,463; 2,322,307; 2,335,017; 2,336,074; 2,339,692; 2,356,043; 2,360,302; 2,362,291; 2,399,877; 2,399,878; 2,409,687; and 2,416,281. A number of such compounds are available as articles of commerce, such as for example, HiTEC® 614 additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.).

Supplemental Antiwear and/or Extreme Pressure Additives.

For certain applications such as use as gear oils, the compositions of this invention will preferably contain one or more oil-soluble supplemental antiwear and/or extreme pressure additives. These comprise a number of well known classes of materials including, for example, sulfur-containing additives, esters of boron acids, esters of phosphorus acids, amine salts of phosphorus acids and acid esters, higher carboxylic acids and derivatives thereof, chlorine-containing additives, and the like.

Typical sulfur-containing antiwear and/or extreme pressure additives include dihydrocarbonyl polysulfides; sulfurole-

5 fins; sulfurized fatty acid esters of both natural (e.g. sperm oil) and synthetic origins; trithiones; thienyl derivatives; sulfurized terpenes; sulfurized oligomers of C₂-C₈ monoolefins; xanthates of alkanols and other organo-hydroxy compounds such as phenols; thiocarbamates made from alkyl amines and other organo amines; and sulfurized Diels-Alder adducts such as those disclosed in U.S. reissue patent Re 27,331. Specific examples include sulfurized polyisobutene of \bar{M}_n 1,150, sulfurized isobutylene, sulfurized triisobutene, dicyclohexyl disulfide, diphenyl and dibenzyl disulfide, di-tert-butyl trisulfide, and dinonyl trisulfide, among others.

Esters of boron acids which may be used include borate, metaborate, pyroborate and baborate esters of monohydric and/or polyhydric alcohols and/or phenols, such as trioctyl borate, tridecyl borate, 2-ethylhexyl pyroborate, isoamyl metaborate, triethyl borate, (butyl)(2,4-hexanediy)borate, and the like.

10 Typical esters of phosphorus acids which may be used as antiwear and/or extreme pressure additives include trihydrocarbyl phosphites, phosphonates and phosphates, and dihydrocarbyl phosphites; such as tricresyl phosphate, tributyl phosphite, tris(2-chloroethyl) phosphate and phosphite, dibutyl trichloromethyl phosphonates, di(n-butyl)phosphite, triphenyl phosphite, tris(tridecyl) phosphite, and tolyl phosphinic acid dipropyl ester.

15 Among the amine salts of phosphorus acids and phosphorus acid-esters which can be employed are amine salts of partially esterified phosphoric, phosphorous, phosphonic, and phosphinic acids and their partial or total thio analogs such as partially esterified monothiophosphoric, dithiophosphoric, trithiophosphoric and tetrathiophosphoric acids; amine salts of phosphonic acids and their thio analogs; and the like. Specific examples include the dihexylammonium salt of dodecylphosphoric acid, the diethyl hexyl ammonium salt of dioctyl dithiophosphoric acid, the octadecylammonium salt of dibutyl thiophosphoric acid, the dilaurylammonium salt of 2-ethylhexylphosphoric acid, the dioleoyl ammonium salt of butane phosphonic acid, and analogous compounds.

20 Higher carboxylic acids and derivatives which can be used as antiwear and/or extreme pressure additives are illustrated by fatty acids, dimerized and trimerized unsaturated natural acids (e.g., linoleic) and esters, amine, ammonia, and metal (particularly lead) salts thereof, and amides and imidazoline salt and condensation products thereof, oxazolines, and esters of fatty acids, such as ammonium di-(linoleic) acid, lard oil, oleic acid, animal glycerides, lead stearate, etc.

25 Suitable chlorine-containing additives include chlorinated waxes of both the paraffinic and microcrystalline type, polyhaloaromatics such as di- and trichlorobenzene, trifluoromethyl naphthalenes, perchlorobenzene, pentachlorophenol and dichloro diphenyl trichloroethane. Also useful are chlorosulfurized olefins and olefinic waxes and sulfurized chlorophenyl methyl chlorides and chloroxanthates. Specific examples include chlorodibenzyl disulfide, chlorosulfurized polyisobutene of \bar{M}_n 600, chlorosulfurized pinene and chlorosulfurized lard oil.

Supplemental Ashless Dispersants.

35 If desired, the compositions of this invention can include one or more supplemental ashless dispersants in order to supplement the dispersancy contributed by component b) (and optional component d) when used). For example, ashless dispersant(s) which differ from component b) and component d) in that the supplemental ashless dispersant(s) are not phosphorylated in the manner of component b) or boronated (and optionally additionally phosphorylated) in the manner of component d) may be used as the supplemental ashless dispersant.

40 Further, use can be made of any of the known carboxylic ashless, hydrocarbyl polyamine, Mannich polyamine, and/or any polymeric polyamine dispersants. Examples of carboxylic ashless dispersants, are described in many patents, including British patent specification No. 1,306,529 and the following U.S. Patents:

3,163,603;	3,184,474;	3,215,707;	3,219,666;	3,271,310;
3,272,746;	3,281,357;	3,306,908;	3,311,558;	3,316,177;
3,340,281;	3,341,542;	3,346,493;	3,381,022;	3,399,141;
45 3,415,750;	3,433,744;	3,444,170;	3,448,048;	3,448,049;
3,451,933;	3,454,607;	3,467,668;	3,522,179;	3,541,012;
3,542,678;	3,574,101;	3,576,743;	3,630,904;	3,632,510;
3,632,511;	3,697,428;	3,725,441;	3,868,330;	3,948,800;
4,234,435;	Re.26,433;	3,172,892;	3,202,678;	3,216,936;
50 3,219,666;	3,254,025;	3,272,746;	4,234,435;	3,331,776;
3,381,022;	3,522,179;	3,184,474;	3,576,743;	3,632,511;
3,804,763;	3,836,471;	3,862,981;	3,936,480;	3,948,800;
3,950,341;	3,957,854;	3,957,855;	3,991,098;	4,071,548;
4,173,540;	and 4,354,950.			

55 Examples of hydrocarbyl polyamine ashless dispersants which may be used are described in U.S. Pat. Nos. 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,671,511; 3,821,302; 3,394,576; and in European Patent Publication No. 382,405.

Examples of Mannich polyamine dispersants which may be used are described in the following U.S. Patents:

2,429,112; 2,962,442; 2,984,550; 3,036,003; 3,166,516; 3,236,770; 3,368,972; 3,413,347; 3,442,808; 3,448,047;
3,454,497; 3,459,661; 3,493,520; 3,539,633; 3,558,743; 3,586,629; 3,591,598; 3,600,372; 3,634,515; 3,649,229;
3,697,574; 3,703,536; 3,704,308; 3,725,277; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202;
3,798,165; 3,798,247; 3,803,039; 3,872,019; 3,980,569; and 4,011,380.

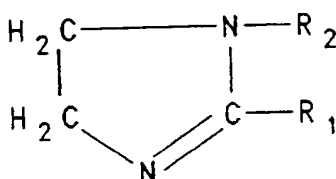
Examples of polymeric polyamine dispersants which may be used are set forth in the following U.S. Patents: 3,316,177; 3,326,804; 3,329,658; 3,449,250; 3,493,520; 3,519,565; 3,666,730; 3,687,849; 3,702,300; 4,089,794; 4,632,769.

4,632,769.

Examples of post-treated ashless dispersants are set forth in the following U.S. Patents: 3,036,003; 3,200,107; 3,216,936; 3,256,185; 3,278,550; 3,312,619; 3,366,569; 3,367,943; 3,373,111; 3,403,102; 3,442,808; 3,455,831; 3,455,832; 3,493,520; 3,502,677; 3,513,093; 3,573,010; 3,579,450; 3,591,598; 3,600,372; 3,639,242; 3,649,229; 3,649,659; 3,702,757; 3,708,522; 4,971,598; 4,820,432; 4,828,742; 4,866,135; 4,866,139; 4,866,140; 4,866,141; 4,866,142; 4,906,394; 4,913,830; 3,184,411; 3,185,645; 3,235,497; 3,265,618; 3,324,032; 3,325,567; 3,403,102; 3,502,677; 3,513,093; 3,511,780; 3,632,985; 3,865,740; 3,950,341; 3,991,056; 4,097,389; 4,234,435; 4,338,205; 4,428,849; 4,615,826; 4,648,980; 4,747,971; and 4,873,004.

The compositions of this invention are imidazoline dispersants

Other ashless dispersants which can be included in the compositions of this invention are imidazoline dispersants which can be represented by the formula:



wherein R₁ represents a hydrocarbon group having 1 to 30 carbon atoms, e.g. an alkyl or alkenyl group having 7 to 22 carbon atoms, and R₂ represents a hydrogen atoms or a hydrocarbon radical of 1 to 22 carbon atoms, or an aminoalkyl, acylaminoalkyl or hydroxyalkyl radical having 2 to 50 carbon atoms. Such long-chain alkyl (or long-chain alkenyl) imidazoline compounds may be made by reaction of a corresponding long-chain fatty acid (of formula R₁-COOH), for example oleic acid, with an appropriate polyamine. The imidazoline formed is then ordinarily called, for example, oleylimidazoline where the radical R₁ represents the oleyl residue of oleic acid. Other suitable alkyl substituents in the 2-position of these imidazolines include undecyl, heptadecyl, lauryl and erucyl. Suitable N-substituents of the imidazolines (i.e. radicals R₂) include hydrocarbonyl groups, hydroxyalkyl groups, aminoalkyl groups, and acylaminoalkyl groups. Examples of these various groups include methyl, butyl, decyl, cyclohexyl, phenyl, benzyl, tolyl, hydroxyethyl, aminoethyl, oleylaminoethyl and stearyl aminoethyl.

Another class of ashless dispersant which can be incorporated in the compositions of this invention are the products of reaction of an ethoxylated amine made by reaction of ammonia with ethylene oxide with a carboxylic acid of 8 to 30 carbon atoms. The ethoxylated amine may be, for example, mono-, di- or tri- ethanolamine or a polyethoxylated derivative thereof, and the carboxylic acid may be, for example, a straight or branched chain fatty acid of 10 to 22 carbon atoms, a naphthenic acid, a resinic acid or an alkyl aryl carboxylic acid.

Still another type of ashless dispersants which can be used in the practice of this invention are the α -olefin-maleimide copolymers such as are described in U.S. Pat. No. 3,909,215. Such copolymers are alternating copolymers of N-substituted maleimides and aliphatic α -olefins of from 8 to 30 carbon atoms. The copolymers may have an average of 4 to 20 maleimide groups per molecule. The substituents on the nitrogen of the maleimide may be the same or different and are organic radicals composed essentially of carbon, hydrogen and nitrogen having a total of 3 to 60 carbon atoms. A commercially available material which is highly suitable for use in this invention is Chevron OFA 425B, and this material is believed to be or comprise an α -olefin maleimide copolymer of the type described in U.S. Pat. No. 3,909,215.

The above and many other types of ashless dispersants can be utilized either singly or in combination in the compositions of this invention, provided of course that they are compatible with the other additive components being employed and are suitably soluble in the base oil selected for use.

Pour Point Depressants.

Another useful type of additive included in compositions of this invention is one or more pour point depressants. The use of pour point depressants in oil-base compositions to improve the low temperature properties of the compositions is well known to the art. See, for example, the books Lubricant Additives by C. V. Smalheer and R. Kennedy Smith (Lezius-Hiles Co. Publishers, Cleveland, Ohio, 1967); Gear and Transmission Lubricants by C. T. Boner (Reinhold Publishing Corp., New York, 1964); and Lubricant Additives by M. W. Ranney (Noyes Data Corporation, New Jersey, 1973). Among the types of compounds which function satisfactorily as pour point depressants in the compositions of

this invention are polymethacrylates, polyacrylates, condensation products of haloparaffin waxes and aromatic compounds, and vinyl carboxylate polymers. Also useful as pour point depressants are terpolymers made by polymerizing a dialkyl fumarate, vinyl ester of a fatty acid and a vinyl alkyl ether. Techniques for preparing such polymers and their uses are disclosed in U.S. Pat. No. 3,250,715. Generally, when they are present in the compositions of this invention, the pour point depressants (on an active content basis) are present in amounts within the range of 0.01 to 5, and more often within the range of 0.01 to 1, weight percent of the total composition.

Viscosity Index Improvers.

Depending upon the viscosity grade required, the lubricant compositions can contain up to 15 weight percent of one or more viscosity index improvers (excluding the weight of solvent or carrier fluid with which viscosity index improvers are often associated as supplied). Among the numerous types of materials known for such use are hydrocarbon polymers grafted with, for example, nitrogen-containing polymers, olefin polymers such as polybutene, ethylene-propylene copolymers, hydrogenated polymers and copolymers and terpolymers of styrene with isoprene and/or butadiene, polymers of alkyl acrylates or alkyl methacrylates, copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminoalkyl methacrylate; post-grafted polymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine; styrene/maleic anhydride polymers post-treated with alcohols and/or amines, and the like.

Dispersant viscosity index improvers, which combine the activity of dispersants and viscosity index improvers, suitable for use in the compositions of this invention are described, for example, in U.S. Pat. Nos. 3,702,300; 4,068,056; 4,068,058; 4,089,794; 4,137,185; 4,146,489; 4,149,984; 4,160,739; and 4,519,929.

Friction Modifiers.

These materials, sometimes known as fuel economy additives, include such substances as the alkyl phosphonates as disclosed in U.S. Pat. No. 4,356,097, aliphatic hydrocarbyl-substituted succinimides derived from ammonia or alkyl monoamines as disclosed in European Patent Publication No. 20037, dimer acid esters as disclosed in U.S. Pat. No. 4,105,571, oleamide, and the like. Such additives, when used are generally present in amounts of 0.1 to 5 weight percent. Glycerol oleates are another example of fuel economy additives and these are usually present in very small amounts, such as 0.05 to 0.2 weight percent based on the weight of the formulated oil.

Other suitable friction modifiers include aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters, aliphatic carboxylic ester-amides, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphates, etc., wherein the aliphatic group usually contains above eight carbon atoms so as to render the compound suitably oil soluble.

A desirable friction modifier additive combination which may be used in the practice of this invention is described in European Patent Publication No. 389,237. This combination involves use of a long chain succinimide derivative and a long chain amide.

Seal Swell Agents.

Additives may be introduced into the compositions of this invention in order to improve the seal performance (elastomer compatibility) of the compositions. Known materials of this type include dialkyl diesters such as dioctyl sebacate, aromatic hydrocarbons of suitable viscosity such as Panasol AN-3N, products such as Lubrizol 730, polyol esters such as Emery 2935, 2936, and 2939 esters from the Emery Group of Henkel Corporation and Hatcol 2352, 2962, 2925, 2938, 2939, 2970, 3178, and 4322 polyol esters from Hatco Corporation. Generally speaking the most suitable diesters include the adipates, azelates, and sebacates of C₈-C₁₃ alkanols (or mixtures thereof), and the phthalates of C₄-C₁₃ alkanols (or mixtures thereof). Mixtures of two or more different types of diesters (e.g., dialkyl adipates and dialkyl azelates, etc.) can also be used. Examples of such materials include the n-octyl, 2-ethylhexyl, isodecyl, and tridecyl diesters of adipic acid, azelaic acid, and sebacic acid, and the n-butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and tridecyl diesters of phthalic acid.

Base Oils.

The additive combinations of this invention can be incorporated in a wide variety of lubricants and functional fluids in effective amounts to provide suitable active ingredient concentrations. The base oils not only can be hydrocarbon oils of lubricating viscosity derived from petroleum (or tar sands, coal, shale, etc.), but also can be natural oils of suitable viscosities such as rapeseed oil, etc., and synthetic oils such as hydrogenated polyolefin oils; poly- α -olefins (e.g., hydrogenated or unhydrogenated α -olefin oligomers such as hydrogenated poly-1-decene); alkyl esters of dicarboxylic

acids; complex esters of dicarboxylic acid, polyglycol and alcohol; alkyl esters of carbonic or phosphoric acids; polysilicones; fluorohydrocarbon oils; and mixtures of mineral, natural and/or synthetic oils in any proportion, etc. The term "base oil" for this disclosure includes all the foregoing.

The additive combinations of this invention can thus be used in lubricating oil and functional fluid compositions, such as automotive crankcase lubricating oils, automatic transmission fluids, gear oils, hydraulic oils, cutting oils, etc., in which the base oil of lubricating viscosity is a mineral oil, a synthetic oil, a natural oil such as a vegetable oil, or a mixture thereof, e.g. a mixture of a mineral oil and a synthetic oil.

Suitable mineral oils include those of appropriate viscosity refined from crude oil of any source including Gulf Coast, Midcontinent, Pennsylvania, California, Alaska, Middle East, North Sea and the like. Standard refinery operations may be used in processing the mineral oil. Among the general types of petroleum oils useful in the compositions of this invention are solvent neutrals, bright stocks, cylinder stocks, residual oils, hydrocracked base stocks, paraffin oils including pale oils, and solvent extracted naphthenic oils. Such oils and blends of them are produced by a number of conventional techniques which are widely known by those skilled in the art.

As is noted above, the base oil can consist essentially of or comprise a portion of one or more synthetic oils. Among the suitable synthetic oils are homo- and interpolymers of C_2 - C_{12} olefins, carboxylic acid esters of both monoalcohols and polyols, polyethers, silicones, polyglycols, silicates, alkylated aromatics, carbonates, thiocarbonates, orthoformates, phosphates and phosphites, borates and halogenated hydrocarbons. Representative of such oils are homo- and interpolymers of C_2 - C_{12} monoolefinic hydrocarbons, alkylated benzenes (e.g., dodecyl benzenes, didodecyl benzenes, tetradecyl benzenes, dinonyl benzenes, di-(2-ethylhexyl)benzenes, wax-alkylated naphthalenes); and polyphenyls (e.g., biphenyls, terphenyls).

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of synthetic oils. These are exemplified by the oils prepared through polymerization of alkylene oxides such as ethylene oxide or propylene oxide, and the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl polyisopropylene glycol ether having an average molecular weight of 1,000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1,000, diethyl ether of polypropylene glycol having a molecular weight of 1,000-1,500) or mono- and poly-carboxylic esters thereof, for example, the acetic acid ester, mixed C_3 - C_6 fatty acid esters, or the C_{13} Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) adipate, didodecyl adipate, di(tridecyl) adipate, di(2-ethylhexyl) sebacate, dilauryl sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, di(eicosyl) sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters which may be used as synthetic oils also include those made from C_3 - C_{18} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol and dipentaerythritol. Trimethylolpropane tripelargonate and pentaerythritol tetracaproate, the ester formed from trimethylolpropane, caprylic acid and sebacic acid, and the polyesters derived from a C_4 - C_{14} dicarboxylic acid and one or more aliphatic dihydric C_3 - C_{12} alcohols such as derived from azelaic acid or sebacic acid and 2,2,4-trimethyl-1,6-hexanediol serve as examples. Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(p-tert-butylphenyl) silicate, poly(methyl)siloxanes, and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, triphenyl phosphite, and diethyl ester of decane phosphonic acid).

Also useful as base oils or as components of base oils are hydrogenated or unhydrogenated liquid oligomers of C_6 - C_{16} alphaolefins, such as hydrogenated or unhydrogenated oligomers formed from 1-decene. Methods for the production of such liquid oligomeric 1-alkene hydrocarbons are known and reported in the literature. See for example U.S. Pat. Nos. 3,749,560; 3,763,244; 3,780,128; 4,172,855; 4,218,330; 4,902,846; 4,906,798; 4,910,355; 4,911,758; 4,935,570; 4,950,822; 4,956,513; and 4,981,578. Additionally, hydrogenated 1-alkene oligomers of this type are available as articles of commerce, for example, under the trade designations ETHYLFLO 162, ETHYLFLO 164, ETHYLFLO 166, ETHYLFLO 168, ETHYLFLO 170, ETHYLFLO 174, and ETHYLFLO 180 poly- α -olefin oils (Ethyl Corporation; Ethyl Canada Ltd.; Ethyl S.A.). Blends of such materials can also be used in order to adjust the viscometrics of the given base oil. Suitable 1-alkene oligomers are also available from other suppliers. As is well known, hydrogenated oligomers of this type contain little, if any, residual ethylenic unsaturation.

Preferred oligomers are formed by use of a Friedel-Crafts catalyst (especially boron trifluoride promoted with water or a C_{1-20} alcohol) followed by catalytic hydrogenation of the oligomer so formed using procedures such as are described in the foregoing U.S. patents.

Other catalyst systems which can be used to form oligomers of 1-alkene hydrocarbons, which, on hydrogenation,

provide suitable oleaginous liquids include Ziegler catalysts such as ethyl aluminum sesquichloride with titanium tetrachloride, aluminum alkyl catalysts, chromium oxide catalysts on silica or alumina supports and a system in which a boron trifluoride catalyzed oligomerization is followed by treatment with an organic peroxide.

It is also possible in accordance with this invention to utilize blends of one or more liquid hydrogenated 1-alkene oligomers in combination with other oleaginous materials having suitable viscosities, provided that the resultant blend has suitable compatibility and possesses the physical properties desired.

Typical natural oils that may be used as base oils or as components of the base oils include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cotton-seed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and the like. Such oils may be partially or fully hydrogenated, if desired.

The fact that the base oils used in the compositions of this invention may be composed of (i) one or more mineral oils, (ii) one or more synthetic oils, (iii) one or more natural oils, or (iv) a blend of (i) and (ii), or (i) and (iii), or (ii) and (iii), or (i), (ii) and (iii) does not mean that these various types of oils are necessarily equivalents of each other. Certain types of base oils may be used in certain compositions for the specific properties they possess such as high temperature stability, non-flammability or lack of corrosivity towards specific metals (e.g. silver or cadmium). In other compositions, other types of base oils may be preferred for reasons of availability or low cost. Thus, the skilled artisan will recognize that while the various types of base oils discussed above may be used in the compositions of this invention, they are not necessarily functional equivalents of each other in every instance.

Proportions and Concentrations

In general, the components of the additive compositions of this invention are employed in the oleaginous liquids (e.g., lubricating oils and functional fluids) in minor amounts sufficient to improve the performance characteristics and properties of the base oil or fluid. The amounts will thus vary in accordance with such factors as the viscosity characteristics of the base oil or fluid employed, the viscosity characteristics desired in the finished product, the service conditions for which the finished product is intended, and the performance characteristics desired in the finished product. However, generally speaking, the following concentrations (weight percent) of the components (active ingredients) in the base oils or fluids are illustrative:

	General Range	Preferred Range	More Preferred Range	Particularly Preferred Range
Component a)	0.1 - 5	0.2 - 2	0.3 - 1.4	0.35 - 1.35
Component b)	0.01 - 20	0.1 - 15	0.5 - 10	1 - 8
Component c)	0 - 20	0.01 - 10	0.1 - 6	0.5 - 3
Component d)	0 - 20	0.1 - 15	0.5 - 10	1 - 8

The relative proportions of components a), b), c) and d) in the finished oleaginous liquids and in the additive concentrates of this invention generally are such that per atom of phosphorus in component b), there are from 0.05 to 100 atoms (and preferably from 0.15 to 10 atoms) of metal as component a); from 0 to 1,000 atoms (and preferably from 0.05 to 150 atoms) of metal as component c); and from 0 to 600 atoms (and preferably from 0.15 to 200 atoms) of boron as component d).

In order to achieve optimum performance, the base oil should contain at least 0.03%, preferably at least 0.04%, more preferably at least 0.05%, and most preferably at least 0.06% by weight of phosphorus as component b). For this reason it is desirable to proportion the components in the additive concentrates to yield such concentrations of phosphorus as component b) at the treat level recommended for any given additive concentrate. A wide variety of component proportions in the additive concentrates can of course be used to achieve these use concentrations in the finished oil. Nevertheless, and without in any way limiting the scope of this invention, preferred additive concentrates of this invention will typically contain at least 0.3% by weight of phosphorus as component b), and may contain as much as 3% or more of phosphorus as component b).

The concentrations (weight percent of active ingredient) of typical optional ingredients in the oleaginous liquid compositions of this invention are generally as follows:

	Typical Range	Preferred Range
Antioxidant	0 - 4	0.05 - 2
Corrosion inhibitor	0 - 3	0.02 - 1
Foam inhibitor	0 - 0.3	0.0002 - 0.1

Continuation of the Table on the next page

(continued)

	Typical Range	Preferred Range
Neutral metal detergent	0 - 3	0 - 2.5
Supplemental antiwear/EP agent	0 - 5	0 - 2
Supplemental ashless dispersant	0 - 10	0 - 5
Pour point depressant	0 - 5	0 - 2
Viscosity index improver	0 - 15	0 - 5
Friction modifier	0 - 3	0 - 1
Seal swell agent	0 - 20	0 - 10
Dye	0 - 0.1	0 - 0.05

The individual components a) and b), preferably component c) and/or component d) as well, and also any and all auxiliary components employed, can be separately blended into the base oil or fluid or can be blended therein in various subcombinations, if desired. Moreover, such components can be blended in the form of separate solutions in a diluent. Except for viscosity index improvers and/or pour point depressants (which are usually blended apart from other components), it is preferable to blend the components used in the form of an additive concentrate of this invention, as this simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the overall concentrate. In this connection, in order to minimize corrosive attack on yellow metals, it is desirable to employ component c) and to arrange the blending order such that components b) and c) are premixed prior to mixing with component a).

The additive concentrates of this invention will contain components a) and b), and preferably components c) and/or d), in amounts proportioned to yield finished oil or fluid blends consistent with the concentrations tabulated above. In most cases, the additive concentrate will contain one or more diluents such as light mineral oils, to facilitate handling and blending of the concentrate. Thus concentrates containing up to 50% by weight of one or more diluents or solvents can be used.

The oleaginous liquids provided by this invention can be used in a variety of applications. For example, they can be employed as crankcase lubricants, gear oils, hydraulic fluids, manual transmission fluids, automatic transmission fluids, cutting and machining fluids, brake fluids, shock absorber fluids, heat transfer fluids, quenching oils, transformer oils, and the like. The compositions are particularly suitable for use as crankcase lubricants for spark ignition (gasoline) engines, and compression ignition (diesel) engines.

Blending

The formulation or blending operations are relatively simple and involve mixing together in a suitable container or vessel, using a dry, inert atmosphere where necessary or desirable, appropriate proportions of the selected ingredients. Those skilled in the art are cognizant of and familiar with the procedures suitable for formulating and blending additive concentrates and lubricant compositions. While it is usually possible to blend the components in various sequences, it is distinctly preferable when forming the concentrates of this invention which are to contain components a), b) and c), to form the concentrate by preblending components b) and c) prior to blending component a) therewith. In this way, the resultant product (whether an additive concentrate or a finished lubricant) is substantially less corrosive to yellow metals, such as copper, than material formed by blending components a) and b) together prior to addition of component c). Similarly, when utilizing a sulfurized fatty ester-polyalkanol amide type product such as SUL-PERM 60-93 as a component, this type of ingredient is preferably introduced into the additive concentrate or into the lubricating oil composition after inclusion therein of at least components a) and b), and, if used, components c) and/or d). In addition, when forming compositions of this invention which are to contain a sulfurized antioxidant or stabilizer and a sulfurized fatty ester-polyalkanol amide type product such as SUL-PERM 60-93, it is preferable to combine the sulfurized antioxidant or stabilizer with the ashless dispersant component(s) prior to mixing with the sulfurized fatty ester-polyalkanol amide type product. It will be appreciated that in any blending operation, the components being blended at any given time should not be irreconcilably incompatible with each other.

Agitation such as with mechanical stirring equipment is desirable to facilitate the blending operation. Frequently it is helpful to apply sufficient heat to the blending vessel during or after the introduction of the ingredients thereto, so as to maintain the temperature at, say, 40-60°C. Similarly, it is sometimes helpful to preheat highly viscous components to a suitable temperature even before they are introduced into the blending vessel in order to render them more fluid and thereby facilitate their introduction into the blending vessel and render the resultant mixture easier to stir or blend. Naturally the temperatures used during the blending operations should be controlled so as not to cause any significant

amount of thermal degradation or unwanted chemical interactions.

When forming the lubricant compositions of this invention, it is usually desirable to introduce the additive ingredients into the base oil with stirring and application of mildly elevated temperatures, as this facilitates the dissolution of the components in the oil and achievement of product uniformity.

The practice and advantages of this invention are still further illustrated by the following examples in which all parts and percentages are by weight unless otherwise specifically indicated. In these examples, the weights of the various ingredients are on an "as received" basis -- i.e., the weights include solvents or diluents which are in the products as supplied. In forming the compositions described in the ensuing examples, the preferred order of addition is to add component a) to a preblend of components b) and c), and in those instances where a sulfurized fatty ester such as SUL-PERM 60-93 is employed, to introduce this component as the final component.

A particularly preferred method of forming such compositions is to form a mixture of components b) and c), or a mixture of components b) and c) plus oil, and heat such mixture for about 15 minutes at 50-60°C. Thereupon all of the other ingredients specified in the examples (except for a sulfurized fatty ester such as SUL-PERM 60-93, if used) can be added in any desired order and the resultant mixture is heated at 50-60°C for about 45 minutes. When a fatty ester such as SUL-PERM 60-93 is used, it is most preferably added as the last component and the resulting composition is heated at 50-60°C for about 10 to 15 minutes. In these operations the mixtures should be stirred throughout.

EXAMPLE I

A crankcase lubricating oil of this invention is formed by blending together the following components:

Component a) ¹	1.20%
Component b) ²	5.00%
Component c) ³	1.40%
Nonylphenol sulfide ⁴	0.25%
Bis(p-nonylphenyl)amine ⁵	0.05%
Antifoam agent ⁶	0.04%
Process oil diluent	1.11%
Viscosity index improver ⁷	5.40%
Sulfurized fatty ester ⁸	0.30%
Neutral calcium sulfonate ⁹	0.25%
Base oil ¹⁰	<u>85.00%</u>
	100.00%

- (1) Zinc dialkyl dithiophosphate (HiTEC® 685 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.; a product having a mixture of alkyl groups formed from 40 mole % 2-propanol, 40 mole % isobutyl alcohol, and 20

mole % 2-ethyl-1-hexanol).

- (2) A product formed as in Example B-6
- (3) Overbased calcium sulfonate (HiTEC® 611 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.; a product having a nominal TBN of 300).
- (4) HiTEC® 619 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.
- (5) Naugalube 438L antioxidant; Uniroyal Chemical Company, Inc.
- (6) Dow Corning Fluid 200; 60,000 cSt, an 8% dimethyl silicone solution from Dow Corning Company.
- (7) Polymethylmethacrylate (Acryloid 954 polymer; Rohm & Haas Chemical Company).
- (8) SUL-PERM 60-93 (Keil Chemical Division of Ferro Corporation).
- (9) HiTEC® 614 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.; a product having a nominal TBN of 30).
- (10) A blend of 51% solvent refined mineral oil (Mobil MTN 736A) and 34% solvent refined mineral oil (Mobil MTN 737).

EXAMPLE II

Using the same ingredients as in Example I except where otherwise indicated, a crankcase lubricating oil of this invention is formed by blending together the following components:

Component a)	0.82%
Component b) ¹	4.00%
Component c)	1.90%
Component d) ²	2.00%
Phenolic antioxidant mixture ³	1.00%
Antifoam agent	0.01%
Pour point depressant ⁴	0.20%
Neutral calcium sulfonate ⁵	1.25%
Process oil diluent	1.29%
Viscosity index improver	5.30%

Base oil⁶

82.23%

100.000%

(1) A product formed as in Example B-9

(2) Boronated succinimide dispersant (HiTEC® 648 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.)

(3) Ethyl® antioxidant 738 diluted to a 50% solution with process oil (Ethyl Corporation; Ethyl Canada Ltd.; Ethyl S.A.).

(4) HiTEC® 672 additive; (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.).

(5) HiTEC® 614 additive; (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.)

(6) A blend of 65.50% Amoco SX-10 and 16.73% Amoco SX-20.

EXAMPLE III

The following components are blended together in the amounts indicated:

Component a)	1.200%
--------------	--------

Component b) ¹	6.000%
---------------------------	--------

Component c)	1.310%
--------------	--------

Nonylphenol sulfide	0.260%
---------------------	--------

Bis(p-nonylphenyl) amine	0.050%
--------------------------	--------

Antifoam agent	0.005%
----------------	--------

Process oil diluent	0.355%
---------------------	--------

Rust inhibitor	0.450%
----------------	--------

Viscosity index improver ²	10.200%
---------------------------------------	---------

Neutral calcium sulfonate	0.320%
---------------------------	--------

Base oil ³	<u>79.850%</u>
-----------------------	----------------

100.000%

(1) A product formed as in Example B-1.

(2) Texas TLA 555 additive (Texaco, Inc., a dispersant-VII copolymer).

(3) Exxon 100 Neutral Low Pour Point oil.

EXAMPLE IV

Using the same ingredients as in Example II except where otherwise indicated, a crankcase lubricating oil of this invention is formed by blending together the following components:

5	Component a)	0.650%
	Component b) ¹	5.360%
	Component c)	1.900%
10	Component d)	2.000%
	Neutral calcium sulfonate	1.250%
	Phenolic antioxidant mixture	1.000%
15	Antifoam agent	0.013%
	Pour point depressant	0.200%
	Viscosity index improver	5.300%
	Process oil diluent	1.287%
20	Base oil ²	<u>81.040%</u>
		100.000%

- - - - -

- 25 (1) A product formed as in Example B-7
- (2) A blend of 64.56% of Amoco SX-10 and 16.48% of Amoco SX-20 oils.

EXAMPLE V

Using the same ingredients as in Example IV except where otherwise indicated, a crankcase lubricating oil of this invention is formed by blending together the following components:

35	Component a)	0.820%
	Component b) ¹	4.000%
	Component c)	1.900%
40	Component d)	2.000%
	Phenolic antioxidant mixture	1.000%
	Antifoam agent	0.013%
45	Pour point depressant	0.200%
	Viscosity index improver	5.300%
	Process oil diluent	2.537%
50	Base oil ²	<u>82.230%</u>

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- 55 (1) A product formed as in Example B-9
- (2) A blend of 65.50% of Amoco SX-10 and 16.73% of Amoco SX-20 oils.

EXAMPLE VI

The procedures of Examples IV and V are repeated except that in each case the phenolic antioxidant mixture is eliminated and replaced by 0.5% of a partially sulfurized mixture of tert-butyl phenols made by reacting Ethyl® antioxidant 733 with sulfur monochloride, for example, as in U.S. Pat. No. 4,946,610, and 0.5% of additional process oil.

EXAMPLE VII

The procedure of Example V is repeated using the same ingredients as therein specified except where otherwise indicated below:

Component a)	1.250%
Component b) ¹	4.690%
Component c)	1.500%
Component d)	2.310%
Nonylphenol sulfide	0.500%
Neutral calcium sulfonate	1.000%
Antifoam agent	0.037%
Sulfurized fatty ester ²	0.500%
Viscosity index improver ³	8.500%
Pour point depressant	0.400%
Process oil diluent	1.583%
Antirust additive ⁴	0.120%
Base oil ⁵	<u>77.610%</u>
	100.000%

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- (1) A product formed as in Example B-6
- (2) SUL-PERM 60-93 (Keil Chemical Division of Ferro Corporation).
- (3) Texaco TLA 656 additive (Texaco, Inc., a dispersant VII olefin copolymer).
- (4) Sterox ND (Monsanto Company), believed to be α -(nonylphenyl)- ω -hydroxy-poly(oxy-1,2-ethanediyl).
- (5) A blend of 50.45% of Mobil MTN 737B and 27.16% of Mobil MTN 736A oils.

EXAMPLE VIII

The procedure of Example VII is repeated using the same ingredients as therein specified except where otherwise indicated below:

EP 0 516 461 B1

Component a)	0.820%
Component b) ¹	3.750%
Component c)	1.860%
Component d)	2.000%
Nonylphenol sulfide	0.520%
Neutral calcium sulfonate	1.150%
Antifoam agent	0.037%
Viscosity index improver ²	0.150%
Antirust additive	0.120%
Process oil diluent	1.573%
Base oil ³	<u>88.020%</u>
	100.000%

- - - - -

- (1) A product formed as in Example B-9
- (2) Paramins ECA 7955 additive (Exxon Chemicals, a division of Exxon Corporation).
- (3) A blend of 73.06% of Ashland 100N and 14.96% of Ashland 330 N solvent refined oils.

EXAMPLE IX

The procedures of Examples VII and VIII are repeated except that in each case the nonyl phenol sulfide is eliminated and replaced by a corresponding amount of a partially sulfurized mixture of tert-butyl phenols described in Example VI.

EXAMPLE X

A synthetic lubricant of this invention is formed by blending together the following components in the amounts specified:

Component a) ¹	0.500%
Component b) ²	6.000%
Component c) ³	1.500%
Neutral calcium sulfonate ⁴	0.500%
Partially sulfurized tert-butyl phenols ⁵	0.500%
Antifoam agent ⁶	0.010%
Antirust additive ⁷	0.150%
Pour point depressant ⁸	0.300%
Process oil diluent	0.710%
Viscosity index improver ⁹	4.200%
Base oil ¹⁰	<u>85.630%</u>
	100.000%

- (1) Zinc dialkyl dithiophosphate (HiTEC® 685 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.; a product having a mixture of alkyl groups formed from 40 mole % 2-propanol, 40 mole % isobutyl alcohol, and 20 mole % 2-ethyl-1-hexanol).
- (2) A product formed as in Example B-9
- (3) Overbased calcium sulfonate (HiTEC® 611 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.; a product having a nominal TBN of 300).
- (4) Neutral calcium sulfonate (HiTEC® 614 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.; a product having a nominal TBN of 30).
- (5) A product formed by reacting ETHYL® Antioxidant 733 with sulfur monochloride, for example as in U.S. Pat. No. 4,946,610.
- (6) Dow Corning Fluid 200; 60,000 cSt, an 8% dimethyl silicone solution from Dow Corning Company.
- (7) Sterox ND (Monsanto Company), believed to be α -(nonyl-phenyl)- ω -hydroxy-poly(oxy-1,2-ethanediyl).
- (8) Santolube C (Monsanto Company).

(9) Texaco TLA 347A additive, (Texaco Inc.).

(10) A blend of 77.26% 8 cSt poly- α -olefin oil (ETHYLFLO 168 oil; Ethyl Corporation; Ethyl Canada Ltd.; Ethyl S.A.) and 8.37% 4 cSt poly- α -olefin oil (Emery 2921 oil; Emery Group of Henkel Corporation).

EXAMPLE XI

The procedure of Example X is repeated except that component b) is prepared as in Example B-1 and is employed at a concentration of 5.940% and the amount of process oil used is 0.770%.

EXAMPLE XII

The procedure of Example X is repeated using the same ingredients except as otherwise specified:

Component a)	0.500%
Component b)	6.000%
Component c)	1.900%
Neutral calcium sulfonate	1.250%
Partially sulfurized tert-butyl phenols	0.750%
Bis(p-nonylphenyl)amine ¹	0.050%
Antifoam agent	0.010%
Antirust additive	0.150%
Process oil diluent	2.050%
Base oil ²	<u>87.340%</u>
	100.000%

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(1) Naugalube 438L antioxidant; Uniroyal Chemical Company, Inc.

(2) A blend of 78.806% 8 cSt poly- α -olefin oil (ETHYLFLO 168 oil; Ethyl Corporation; Ethyl Canada Ltd.; Ethyl S.A.) and 8.534% 40 cSt poly- α -olefin oil (ETHYLFLO 174 oil; Ethyl Corporation; Ethyl Canada Ltd.; Ethyl S.A.).

EXAMPLE XIII

The procedure of Example XII is repeated using the same ingredients except where otherwise specified:

Component a)	0.500%
Component b)	6.000%
Component c)	1.900%
Neutral calcium sulfonate	1.250%
Partially sulfurized tert-butyl phenols	0.750%
Bis(p-nonylphenyl)amine	0.050%
Antifoam agent	0.010%
Viscosity index improver ¹	7.200%
Process oil diluent	0.260%
Base oil ²	<u>82.080%</u>
	100.000%

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(1) Paratone 715 (Exxon Chemical Company).

(2) A blend of 69.77% 8 cSt poly- α -olefin oil (ETHYLFLO 168 oil; Ethyl Corporation; Ethyl Canada Ltd.; Ethyl S.A.) and 12.31% 40 cSt poly- α -olefin oil (ETHYLFLO 174 oil; Ethyl Corporation; Ethyl Canada Ltd.; Ethyl S.A.).

EXAMPLE XIV

An additive concentrate of this invention is formed by blending together the following components as identified in Example I:

Component a)	12.50%
Component b)	52.08%
Component c)	14.58%
Neutral calcium sulfonate	2.60%
Nonylphenol sulfide	2.60%
Bis(p-nonylphenyl)amine	0.52%
Antifoam agent	0.42%
Sulfurized fatty ester	3.13%
Process oil diluent	11.57%
	<u>100.00%</u>

EXAMPLE XV

An additive concentrate of this invention is formed by blending together the following components as identified in Example II:

Component a)	6.11%
Component b)	38.33%
Component c)	14.17%
Component d)	14.91%
Phenolic antioxidant mixture	7.46%

Continuation of the Table on the next page

EP 0 516 461 B1

(continued)

Neutral calcium sulfonate	9.32%
Antifoam agent	0.07%
Process oil diluent	9.63%
	<u>100.00%</u>

EXAMPLE XVI

An additive concentrate of this invention is formed by blending together the following components as identified in Example IV:

Component a)	4.83%
Component b)	39.82%
Component c)	14.12%
Component d)	14.86%
Neutral calcium sulfonate	9.29%
Phenolic antioxidant mixture	7.43%
Antifoam agent	0.10%
Process oil diluent	9.55%
	<u>100.00%</u>

EXAMPLE XVII

An additive concentrate of this invention is formed by blending together the following components as identified in Example V:

Component a)	6.68%
Component b)	32.60%
Component c)	15.48%
Component d)	16.30%
Phenolic antioxidant mixture	8.15%
Antifoam agent	0.11%
Process oil diluent	<u>20.68%</u>
	<u>100.00%</u>

EXAMPLE XVIII

An additive concentrate of this invention is formed by blending together the following components as identified in Example VII:

Component a)	9.27%
Component b)	34.77%
Component c)	11.12%
Component d)	17.12%
Nonyl phenol sulfide	3.71%
Neutral calcium sulfonate	7.41%
Antifoam agent	0.27%
Sulfurized fatty ester	3.71%

Continuation of the Table on the next page

(continued)

Antirust additive	0.89%
Process oil diluent	11.73%
	<u>100.00%</u>

EXAMPLE XIX

An additive concentrate of this invention is formed by blending together the following components as identified in Example VIII:

Component a)	6.93%
Component b)	31.70%
Component c)	15.72%
Component d)	16.91%
Nonyl phenol sulfide	4.40%
Neutral calcium sulfonate	9.72%
Antifoam agent	0.31%
Antirust additive	1.01%
Process oil diluent	13.30%
	<u>100.00%</u>

EXAMPLE XX

An additive concentrate of this invention is formed by blending together the following components:

Component a)¹

5.81%

Component b) ²	75.60%
Component c) ³	14.43%
5 Nonyl phenol sulfide ⁴	2.81%
Bis(p-nonylphenyl)amine ⁵	0.50%
Antifoam agent ⁶	0.05%
10 Process oil diluent	<u>0.80%</u>
	100.00%

- - - - -

15 (1) Zinc dialkyl dithiophosphate (HiTEC® 685 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.; a product having a mixture of alkyl groups formed from 40 mole % 2-propanol, 40 mole % isobutyl alcohol, and 20 mole % 2-ethyl-1-hexanol).

(2) A product formed as in Example B-5

25 (3) Overbased calcium sulfonate (HiTEC® 611 additive; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.; a product having a nominal TBN of 300).

30 (4) HiTEC® 619 additive; (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.).

(5) Naugalube 438L antioxidant; Uniroyal Chemical Company, Inc.

35 (6) Dow Corning Fluid 200; 60,000 cSt, an 8% dimethyl silicone solution from Dow Corning Company.

40 A lubricant composition of this invention is formed by blending the above concentrate and a viscosity index improver in a base oil as follows:

Above additive concentrate	9.979%
Viscosity index improver ¹	7.000%
45 Base oil ²	<u>83.021%</u>
	100.000%

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50 (1) Polymethylmethacrylate viscosity index improver (Acryloid 953 polymer; Rohm & Haas Chemical Company).

55 (2) A blend of 62.05% Turbine 5 oil (a 100 Solvent Neutral refined mineral oil) and 20.971% Esso Canada MCT-10 oil (a 150 Solvent Neutral refined mineral oil).

EXAMPLE XXI

An additive concentrate of this invention is formed by blending together the components as identified in Example XX, except as otherwise indicated, in the following proportions:

Component a)	6.68%
Component b) ¹	32.60%
Component c)	15.48%
Component d) ²	16.30%
Antifoam agent	0.11%
Phenolic antioxidant mixture ³	8.15%
Process oil diluent	<u>20.68%</u>
	100.00%

- - - - -

- (1) A product formed as in Example B-9
- (2) HiTEC® 648 additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.).
- (3) Ethyl® Antioxidant 738 (Ethyl Corporation; Ethyl Canada Ltd.; Ethyl S.A.) diluted to a 50% solution in process oil.

A lubricant composition of this invention is formed by blending the above concentrate, a viscosity index improver, and a pour point depressant in a base oil described below:

Above additive concentrate	12.270%
Viscosity index improver ¹	5.300%
Pour point depressant ²	0.200%
Base oil ³	<u>82.230%</u>
	100.000%

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- (1) Polymethacrylate viscosity index improver (Acryloid 954 polymer; Rohm & Haas Chemical Company).
- (2) Sterox ND (Monsanto Company), believed to be α -(nonyl-phenyl)- ω -hydroxy-poly(oxy-1,2-ethanediyl).
- (3) A blend of 65.504% of Amoco SX-10 and 16.726% of Amoco SX-20 oils.

EXAMPLE XXII

A lubricant of this invention is formed by blending together the components as identified in Example XXI, except as otherwise indicated, in the following proportions:

	Component a)	0.880%
	Component b) ¹	3.000%
5	Component c)	1.900%
	Component d) ²	2.330%
	Component d) ³	0.670
	Neutral calcium sulfonate ⁴	1.250%
10	Antifoam agent	0.013%
	Bis(p-nonylphenyl)amine ⁵	0.050%
	Phenolic antioxidant mixture	1.000%
15	Process oil diluent	1.287%
	Pour point depressant ⁶	0.200%
	Viscosity index improver ⁷	10.700%
		<u>76.720%</u>
20	Base oil ⁸	100.00%

- - - - -

- (1) A product formed as in Example B-6
- (2) A product formed as in Example B-4
- (3) HiTEC® 648 additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.).
- (4) HiTEC® 614 additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.).
- (5) Naugalube 438L antioxidant; Uniroyal Chemical Company, Inc.
- (6) Sterox ND (Monsanto Company), believed to be α -(nonylphenyl)- ω -hydroxy-poly(oxy-1,2-ethanediyl).
- (7) Amoco 6565 viscosity index improver.
- (8) A blend of 56.006% of Amoco SX-10 and 20.714% of Amoco SX-20 oils.

The lubricating oil compositions of Examples I and II were subjected to the standard Sequence VE engine test procedure. The results of this evaluation are summarized in the following table, which also shows the American Petroleum Institute SG passing limits for the various parameters.

Table

- Sequence VE Test Results			
Rating	This Invention		API SG Limits
Engine Cleanliness	Example I	Example II	
Average Sludge	9.32	9.40	9.0 min.
Average Varnish	6.56	6.95	5.0 min.
Rocker Arm Cover Sludge	8.65	8.70	7.0 min.
Piston Skirt Varnish	6.91	7.04	6.5 min.
Engine Wear			
Average Cam Lobe Wear, mils	2.14	0.52	5.0 max.
Maximum Cam Lobe Wear, mils	6.40	0.70	15.0 max.

The antiwear advantages that can be achieved by the practice of this invention were further illustrated by a series of standard 4-Ball wear tests (40 kg load, 1800 rpm, 54.4°C (130°F), 30 minute test length) on three lubricating oil compositions having the same total concentration of phosphorus therein. The compositions were identical to each other except that one such composition (Oil A) contained only zinc dialkyldithiophosphate as the phosphorus-containing component whereas another such composition (Oil B) contained a phosphorylated succinimide of this invention as the sole source of phosphorus. Oil C, a representative composition of this invention, contained the combination of both the same zinc dialkyldithiophosphate and the same phosphorylated succinimide dispersant. All compositions contained in addition the same concentration of overbased calcium sulfonate having a nominal TBN of 300. The makeup of these compositions was as follows:

Oil A

- 1.18 grams of zinc dialkyldithiophosphate¹
 1.23 grams of overbased calcium sulfonate²
 97.59 grams of mineral oil³

Oil B

- 10.29 grams of phosphorylated succinimide⁴
 1.23 grams of overbased calcium sulfonate²
 88.48 grams of mineral oil³

Oil C

- 0.59 grams of zinc dialkyldithiophosphate¹
 5.14 grams of phosphorylated succinimide⁴
 1.23 grams of overbased calcium sulfonate²
 93.04 grams of mineral oil³

- (1) HiTEC® 685 Additive (Ethyl Petroleum Additives, Inc.;
 Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl
 Canada Ltd.)
 (2) HiTEC® 611 Additive (Ethyl Petroleum Additives, Inc.;
 Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl
 Canada Ltd.)
 (3) Turbine 5 oil, a 100 Solvent Neutral refined mineral
 oil.
 (4) Prepared as in Example B-9

The results of these 4-Ball tests were as follows:

Composition	Scar Diameter, mm
Oil A	0.433
Oil B	0.608
Oil C	0.416

In another pair of 4-Ball Tests, two blends were formed from the same base oil. Blend A contained the following:

- 1.2% of zinc dialkyldithiophosphate¹
 1.3% of overbased calcium sulfonate²
 0.5% of sulfurized fatty ester³
 6.0% of non-phosphorylated, non-boronated succinimide⁴

Blend B contained the following:

- 1.2% of zinc dialkyldithiophosphate¹
 1.3% of overbased calcium sulfonate²
 0.5% of sulfurized fatty ester³
 7.5% of phosphorylated, non-boronated succinimide⁵

- (1) HiTEC® 685 Additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.).
- (2) HiTEC® 611 Additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.).
- (3) SUL-PERM 60-93 (Keil Chemical Division of Ferro Corporation).
- (4) Polyisobutenyl succinimide derived from polyisobutene with Mn of 1300 and a mixture of polyethylene polyamines with an overall composition approximating that of tetraethylene pentamine).
- (5) Product formed as in Example B-7

The results of these 4-Ball tests were as follows:

Composition	Scar Diameter, mm
Blend A	0.437
Blend B	0.372

The ability of overbased alkali or alkaline earth metal-containing detergents to suppress copper corrosion was demonstrated by a pair of tests employing a base oil (Turbine 5 oil) containing in one instance components a), b) and c) and in another instance omitting component c) from the composition. These tests were conducted according to ASTM D-130 but under more severe conditions, viz., operation at 121°C rather than at the standard temperature of 100°C. In these tests component a) was HiTEC® 685 additive (a zinc dialkyl dithiophosphate described above), component b) was formed as in Example B-7, and component c) was HiTEC® 611 additive (an overbased calcium sulfonate). The compositions tested (weight percentages) and the results obtained therewith are tabulated below:

Compositions	Run 1	Run 2
Component a)	0.65	0.65
Component b)	5.36	5.36
Component c)	--	1.90
Base oil	93.99	92.09
Results:	4b	1b/2a with trace of 2d

Another pair of D-130 tests was conducted as above using the same materials as components a), b) and in one

instance, c). The makeup of the compositions tested and the test results were as follows:

<u>Compositions</u>	<u>Run 1</u>	<u>Run 2</u>
Component a)	0.77	0.77
Component b)	3.00	3.00
Component c)	--	1.40
Component d) ¹	2.00	2.00
Neutral calcium sulfonate ²	0.30	0.30
Antifoam agent ³	0.01	0.01
Process oil	0.62	0.62
Base oil ⁴	93.30	91.90
<u>Results:</u>	4a	1a

(1) HiTEC® 648 Additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.).

(2) HiTEC® 614 Additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Ltd.).

(3) Dow Corning Fluid 200; 60,000 cSt, an 8% dimethyl silicone solution from Dow Corning Company.

(4) Turbine 5 oil.

Still another series of D-130 Tests conducted as above using the same materials as above for components a), b) and c), demonstrated the fact that the beneficial effects on reduced copper corrosivity engendered by use of a metal-containing detergent of relatively high TBN are realized over a wide range of proportions. The makeup of the test compositions and the results obtained are summarized in the following table:

Compositions	Run 1	Run 2	Run 3	Run 4
Component a)	0.77	0.77	0.77	0.77
Component b)	5.00	4.00	3.00	2.00
Component c)	1.40	1.40	1.40	1.40
Base oil	92.83	93.83	94.83	95.83
<u>Results:</u>	1b	1a	1a	1a

Another feature of this invention is that the particularly preferred phosphorylated alkenyl succinimides of polyethylene polyamines made from alkenyl succinic anhydrides (or like succinic acylating agents, such as the acid, acid halide, lower alkyl ester, lower alkyl-acid ester) in which the succination ratio (i.e., ratio of the average number of succinic groups per alkenyl group chemically bound in the acylating agent) is in the range of 1:1 to 1.3:1 and in which the alkenyl group is derived from a polyolefin having a number average molecular weight in the range of 600 to 1,300 (preferably 700 to 1,200, and most preferably 800 to 1,100) when utilized in accordance with this invention can provide greater dispersancy than the same concentration or an even higher concentration of an analogous succinimide not containing phosphorus or an analogous boronated succinimide not containing phosphorus.

For example, a group of lubricant compositions made from different succinimide dispersants were subjected to a bench test simulating sludge performance in the Sequence VE engine tests. This test involves subjecting each lubricant to standard Hot Oil Oxidation Test (HOOT) conditions and determining the change in dielectric constant of the lubricants

before and after the oxidation. On completion of the oxidation, the oxidized oil is mixed with a known amount of standard oxidized oil (a laboratory preparation) and diluted with a hydrotreated base stock. Turbidity measurements are then taken and then dielectric constant measurement, HOOT time and turbidity data, are combined into a single number for reporting and comparison purposes. A lower number indicates better anti-sludge properties.

The lubricant compositions subjected to this test were as described in Example III except that component b) was varied as indicated in the following table. The results of these tests were as follows:

<u>Run No.</u>	<u>Succinimide Dispersant Used</u>	<u>Bench Test Sludge Factor</u>
1	Phosphorylated ($\bar{M}_n = 950$) ¹	62.6
2	Phosphorylated ($\bar{M}_n = 950$) ²	290.0
3	Phosphorylated ($\bar{M}_n = 950$) ³	68.9
4	Phosphorylated ($\bar{M}_n = 1300$) ⁴	65.8
5	Phosphorylated ($\bar{M}_n = 1300$) ⁵	492.0
6	Phosphorylated ($\bar{M}_n = 1300$) ⁶	71.2

- (1) Produced as in Example B-9
- (2) Produced as in Example B-22
- (3) Produced as in Example B-20
- (4) Produced as in Example B-7
- (5) Produced as in Example B-23
- (6) Produced as in Example B-8

The results tabulated above indicate, among other things, that when the finished oil contained significantly less than 0.03% by weight of phosphorus as component b) in the particular formulation tested (Run Nos. 2 and 5), optimum results were not achieved. Putting the matter a different way, these results indicate that on an equal weight basis the component b) materials produced as in Examples B-7, B-8 B-9, and B-20 were substantially more effective than those produced as in Examples B-22 and B-23.

Data further illustrating the effectiveness of various embodiments of this invention under various test conditions are summarized below.

An SAE 15W40 lubricant of this invention formulated as in Example V was subjected to the Toyota 3AU test procedure to assess valve train wear. After 100 hours a rocker arm demerit rating of 22.2 was obtained.

An SAE 15W40 lubricant of this invention formulated as in Example XXII was subjected to the Sequence VE test procedure. The results were as follows:

Rating	
Average Sludge	9.29
Average Varnish	6.27
Rocker Arm Cover Sludge	8.68
Piston Skirt Varnish	6.82
Engine Wear	
Average Cam Lobe Wear, mils	0.98
Maximum Cam Lobe Wear, mils	2.10

This same composition was subjected to the L-38 test and gave a bearing weight loss of only 14.8 mg. The limit for passing the test is 40 mg.

Rendering the results achievable by the practice of this invention all the more remarkable is the fact that in U.S. Pat. No. 4,873,004 it is pointed out that to achieve improved dispersancy properties it is necessary to have a molar ratio of succinic groups to alkenyl groups (sometimes referred to as the "succination ratio") of at least 1.4 when using succinimides made from polyamines such as tetraethylene pentamine and polyisobutenyl succinic anhydrides having number average molecular weights in the range of 600 to 1,300. For example the patent shows in its Tables 3 and 4 that with succinimide derived from polyisobutylene of number average molecular weight of 950, maleic anhydride and tetraethylene pentamine, products having a succination ratio of 1.0 gave inferior results on dispersancy and varnish formation than corresponding succinimides in which the succination ratio was 1.8. Yet as shown by some of the results presented above, phosphorylated polyisobutenyl succinimides with a succination ratio of 1.18 made from polyisobutene of number average molecular weight of about 950, gave excellent results both on dispersancy and on wear prevention.

As used in the foregoing description, the term "oil-soluble" is used in the sense that the component in question has sufficient solubility in the selected base oil in order to dissolve therein at ordinary temperatures to a concentration at least equivalent to the minimum concentration specified herein for use of such component. Preferably, however, the solubility of such component in the selected base oil will be in excess of such minimum concentration, although there is no requirement that the component be soluble in the base oil in all proportions. As is well known to those skilled in the art, certain useful additives do not completely dissolve in base oils but rather are used in the form of stable suspensions or dispersions. Additives of this type can be employed in the compositions of this invention, provided they do not significantly interfere with the performance or usefulness of the composition in which they are employed.

Claims

1. An additive concentrate composition which comprises:

- (a) one or more oil-soluble metal hydrocarbyl dithiophosphates or dithiocarbamates; and
- (b) one or more oil-soluble boron-free additive compositions formed by heating

- (i) at least one boron-free oil-soluble ashless dispersant comprising at least one acyclic hydrocarbyl-substituted succinimide formed from a mixture of ethylene polyamines having an approximate overall composition falling in the range corresponding to diethylene triamine to pentaethylene hexamine, and wherein said succinimide contains at least basic nitrogen, with
- (ii) phosphorous acid, H_3PO_3 , such that a liquid boron-free phosphorus-containing composition is formed.

2. A composition according to claim 1 wherein component (a) comprises one or more oil-soluble zinc dihydrocarbyl dithiophosphates; and wherein the relative proportions of components (a) and (b) are such that the atom ratio of phosphorus in the form of component (a) to phosphorus in the form of component (b), respectively, falls in the range of 5:1 to 0.1:1.

3. A composition according to claim 2 wherein component (a) comprises one or more oil-soluble zinc dialkyl dithiophosphates; and wherein the relative proportions of components (a) and (b) are such that the atom ratio of phosphorus in the form of component (a) to phosphorus in the form of component (b), respectively, falls in the range of 4:1 to 1:1.

4. A composition according to any one of claims 1 to 3 further comprising (c) at least one oil-soluble alkali or alkaline earth metal-containing detergent, preferably a sulfonate detergent, the relative proportions of the components of said composition being such that per atom of phosphorus in said component (b), there are from 0.15 to 10 atoms of metal as component (a) and from 0.05 to 150 atoms of alkali or alkaline earth metal as component (c).
5. A composition according to claim 3 wherein component (c) has a TBN of at least 50, preferably at least 300.
6. A composition according to claim 4 or 5 wherein said detergent is at least one overbased calcium sulfonate detergent or at least one overbased magnesium sulfonate detergent, or a combination of said overbased detergents.
7. A composition according to any one of claims 1 to 6 further comprising (d) at least one oil-soluble or oil-dispersible boron-containing compound, the relative proportions of the components of said composition being such that per atom of phosphorus in said component (b), there are from 0.15 to 10 atoms of metal as component (a) and from 0.15 to 200 atoms of boron as component (d).
8. A composition according to claim 7 wherein component (d) is at least one oil-soluble boron- and phosphorus-containing ashless dispersant.
9. A composition according to any of the foregoing claims further comprising at least one oil-soluble antioxidant and at least one corrosion inhibitor.
10. A lubricant or functional fluid composition which comprises a major proportion of at least one oil of lubricating viscosity and a minor proportion of the components of a composition according to any one of the foregoing claims.
11. A composition in accordance with claim 10 wherein the total amount of said components (a) and (b) is in the range of 0.3% to 17% by weight based on the total weight of the composition.
12. A method of forming a blend comprising the following components:
 - (a) one or more oil-soluble metal hydrocarbyl dithiophosphates or dithiocarbamates;
 - (b) one or more oil-soluble boron-free additive compositions formed by heating (i) at least one boron-free oil-soluble ashless dispersant containing at least one acyclic hydrocarbyl-substituted succinimide formed from a mixture of ethylene polyamines having an approximate overall composition falling in the range corresponding to diethylene triamine to pentaethylene hexamine, and wherein said succinimide contains at least basic nitrogen, with (ii) phosphorus acid, H_3PO_3 , such that a liquid boron-free phosphorus-containing composition is formed; and
 - (c) one or more oil-soluble alkali or alkaline earth metal-containing detergents having a TBN of at least about 50;said method comprising mixing said component (a) with a preformed mixture comprising said components (b) and (c).
13. The use of a lubricant or functional fluid composition according to claim 10 or 11 in a mechanical mechanism, preferably an internal combustion engine or a vehicular transmission, in which said composition is in contact with an elastomeric material, especially a fluoroelastomer.

Patentansprüche

1. Additivkonzentratzusammensetzung, enthaltend:

- (a) ein oder mehrere öllösliche Metallhydrocarbyldithiophosphate oder -dithiocarbamate und
- (b) ein oder mehrere öllösliche borfreie Additivzusammensetzungen, erhalten durch Erhitzen von
- (i) mindestens einem borfreien öllöslichen aschefreien Dispergiermittel, das mindestens ein durch acyclisches Hydrocarbyl-substituiertes Succinimid enthält, das aus einem Gemisch aus Ethylenpolyaminen mit einer ungefähren Gesamtzusammensetzung, die in den Diethylentriamin bis Pentaethylenhexamin entsprechenden Bereich fällt, erhalten wird, wobei das Succinimid mindestens basischen Stickstoff enthält, mit

(ii) Phosphorsäure (H_3PO_3),
sodaß sich eine flüssige borfreie phosphorhaltige Zusammensetzung bildet.

2. Zusammensetzung gemäß Anspruch 1, in der die Komponente (a) ein oder mehr öllösliche Zinkdihydrocarbyldithiophosphate enthält und die relativen Anteile der Komponenten (a) und (b) so gewählt sind, daß das Atomverhältnis von Phosphor in Form der Komponente (a) zu Phosphor in Form der Komponente (b) im Bereich von 5:1 bis 0,1 : 1 liegt.
3. Zusammensetzung gemäß Anspruch 2, in der die Komponente (a) ein oder mehr öllösliche Zinkdialkyldithiophosphate enthält und die relativen Anteile der Komponenten (a) und (b) so gewählt sind, daß das Atomverhältnis von Phosphor in Form der Komponente (a) zu Phosphor in Form der Komponente (b) im Bereich von 4:1 bis 1:1 liegt.
4. Zusammensetzung gemäß einem der Ansprüche 1 bis 3, die zusätzlich (c) mindestens ein öllösliches, ein Alkali- oder Erdalkalimetall enthaltendes Detergenz, vorzugsweise ein Sulfonatdetergenz enthält, wobei die relativen Anteile der Komponenten dieser Zusammensetzung so gewählt sind, daß pro Atom Phosphor in der Komponente (b) 0,15 bis 10 Metallatome als Komponente (a) und 0,05 bis 150 Atome Alkali- oder Erdalkalimetall als Komponente (c) vorhanden sind.
5. Zusammensetzung gemäß Anspruch 3, in der die Komponente (c) eine Gesamtbasenzahl (TBN = total base number) von mindestens 50, vorzugsweise von mindestens 300 aufweist.
6. Zusammensetzung gemäß Anspruch 4 oder 5, in der das Detergenz mindestens ein überbasisches Calciumsulfonatdetergenz, mindestens ein überbasisches Magnesium-sulfonatdetergenz oder eine Kombination dieser überbasischen Detergenzien ist.
7. Zusammensetzung gemäß einem der Ansprüche 1 bis 6, die zusätzlich (d) mindestens eine öllösliche oder eine in Öl dispergierbare borhaltige Komponente enthält, wobei die relativen Anteile der Komponenten dieser Zusammensetzung so gewählt sind, daß pro Atom Phosphor in Komponente (b) 0,15 bis 10 Atome Metall als Komponente (a) und 0,15 bis 200 Atome Bor als Komponente (d) vorliegen.
8. Zusammensetzung gemäß Anspruch 7, in der die Komponente (d) mindestens ein öllösliches Bor und Phosphor enthaltendes aschefreies Dispergiemittel ist.
9. Zusammensetzung gemäß einem der vorstehenden Ansprüche, die zusätzlich mindestens ein öllösliches Antioxidans und mindestens einen Korrosionsinhibitor enthält.
10. Schmiermittel oder funktionale Fluidzusammensetzung, die einen Hauptanteil mindestens eines Öls mit Schmierviskosität und einen kleineren Anteil der Komponenten einer Zusammensetzung gemäß einem der vorstehenden Ansprüche enthält.
11. Zusammensetzung gemäß Anspruch 10, in der die Gesamtmenge der Komponenten (a) und (b) im Bereich von 0,3 bis 17 Gew.-%, bezogen auf das Gesamtgewicht der Zusammensetzung, liegt.
12. Verfahren zur Herstellung eines Gemisches mit den folgenden Komponenten:
 - (a) einem oder mehreren öllöslichen Metallhydrocarbyldithiophosphonaten oder -dithiocarbamaten,
 - (b) einem oder mehreren öllöslichen borfreien Additivzusammensetzungen, erhalten durch Erhitzen- von
 - (i) mindestens einem borfreien, öllöslichen aschefreien Dispergiemittel, das mindestens ein durch acyclisches Hydrocarbyl-substituiertes Succinimid enthält, das aus einem Gemisch aus Ethylenpolyaminen mit einer ungefähren Gesamtzusammensetzung, die in den Diethylentriamin bis Pentaethylenhexamin entsprechenden Bereich fällt, erhalten wird, wobei das Succinimid mindestens basischen Stickstoff enthält, mit
 - (ii) Phosphorsäure (H_3PO_3),
sodaß sich eine flüssige borfreie phosphorhaltige Zusammensetzung bildet, und
 - (c) einem oder mehreren öllöslichen, Alkali- oder Erdalkalimetall enthaltenden Detergenzien mit einer Gesamtbasenzahl (TBN) von mindestens etwa 50, wobei das Verfahren aus dem Mischen der Komponente (a) mit

einer zuvor gebildeten Mischung aus den Komponenten (b) und (c) besteht.

13. Verwendung eines Schmiermittels oder einer einer funktionellen Fluidzusammensetzung gemäß Anspruch 10 oder 11 in einer mechanischen Vorrichtung, vorzugsweise einer Verbrennungskraftmaschine oder einem Fahrzeuggetriebe, bei der diese Zusammensetzung in Kontakt mit einem elastomeren Material, insbesondere einem Fluorelastomer steht.

Revendications

1. Composition concentrée d'additifs, qui comprend :

- (a) un ou plusieurs hydrocarbyle-dithiophosphates ou -dithiocarbamates métalliques solubles dans l'huile ; et
- (b) une ou plusieurs compositions d'additifs ne contenant pas de bore, solubles dans l'huile, formées par chauffage
 - (i) d'au moins un dispersant sans cendres soluble dans l'huile ne contenant pas de bore, comprenant au moins un succinimide à substituant hydrocarbyle acyclique formé à partir d'un mélange d'éthylène-polyamines dont la composition globale approximative se situe dans la plage allant de la diéthylènetriamine à la pentaéthylènehexamine, et dans lesquelles le succinimide contient au moins de l'azote basique, avec
 - (ii) de l'acide phosphoreux H_3PO_3 , de manière à former une composition liquide contenant du phosphore et ne contenant pas de bore.

2. Composition suivant la revendication 1, dans laquelle le composant (a) comprend un ou plusieurs dihydrocarbyle-dithiophosphates de zinc solubles dans l'huile ; et les proportions relatives de composants (a) et (b) sont choisies de manière que le rapport atomique du phosphore sous la forme du composant (a) au phosphore sous la forme du composant (b) se situe dans la plage de 5:1 à 0,1:1.

3. Composition suivant la revendication 2, dans laquelle le composant (a) comprend un ou plusieurs dialkyl-dithiophosphates de zinc solubles dans l'huile ; et dans laquelle les proportions relatives des composants (a) et (b) sont telles que le rapport atomique du phosphore sous la forme du composant (a) au phosphore sous la forme du composant (b) se situe dans la plage de 4:1 à 1:1.

4. Composition suivant l'une quelconque des revendications 1 à 3, comprenant en outre (c) au moins un détergent soluble dans l'huile contenant un métal alcalin ou un métal alcalino-terreux, de préférence un détergent du type sulfonate, les proportions relatives des composants de cette composition étant telles qu'il y ait, par atome de phosphore présent dans le composant (b), 0,15 à 10 atomes de métal comme composant (a) et 0,05 à 150 atomes de métal alcalin ou alcalino-terreux comme composant (c).

5. Composition suivant la revendication 3, dans laquelle le composant (c) a un indice de basicité totale d'au moins 50, de préférence d'au moins 300.

6. Composition suivant la revendication 4 ou 5, dans laquelle le détergent est au moins un détergent formé de sulfonate de calcium rendu surbasique ou au moins un détergent formé de sulfonate de magnésium rendu surbasique ou une association de ces détergents rendus surbasiques.

7. Composition suivant l'une quelconque des revendications 1 à 6, comprenant en outre (d) au moins un composé contenant du bore soluble ou dispersable dans l'huile, les proportions relatives des composants de la composition étant telles que, pour chaque atome de phosphore dans le composant (b), il y ait 0,15 à 10 atomes de métal comme composant (a) et 0,15 à 200 atomes de bore comme composant (d).

8. Composition suivant la revendication 7, dans laquelle le composant (d) est au moins un dispersant sans cendres soluble dans l'huile contenant du bore et du phosphore.

9. Composition suivant l'une quelconque des revendications précédentes, comprenant en outre au moins un antioxydant soluble dans l'huile et au moins un inhibiteur de corrosion.

10. Composition de lubrifiant ou de fluide fonctionnel, qui comprend une proportion dominante d'au moins une huile de viscosité propre à la lubrification et une quantité secondaire des composants d'une composition suivant l'une quelconque des revendications précédentes.

5 11. Composition suivant la revendication 10, dans laquelle la quantité totale des composants (a) et (b) se situe dans la plage de 0,3 % à 17 % en poids sur la base du poids total de la composition.

12. Procédé pour former un mélange comprenant les composants suivants :

10 (a) un ou plusieurs hydrocarbyle-dithiophosphates ou -dithiocarbamates métalliques solubles dans l'huile,
(b) une ou plusieurs compositions d'additifs dépourvues de bore, solubles dans l'huile, formées par chauffage
(i) d'au moins un dispersant sans cendres soluble dans l'huile dépourvu de bore, contenant au moins un succinimide à substituant hydrocarbyle acyclique formé à partir d'un mélange d'éthylènapolyamines ayant une composition globale approximative comprise dans la plage allant de la diéthylènetriamine à la pentaéthylènehexamine, et dans lesquelles le succinimide contient au moins de l'azote basique, avec

15 (ii) de l'acide phosphoreux H_3PO_3 , de manière à former une composition liquide contenant du phosphore dépourvue de bore ; et

20 (c) un ou plusieurs détergents solubles dans l'huile contenant un métal alcalin ou un métal alcalino-terreux, ayant un indice de basicité totale au moins égal à environ 50 ;

ce procédé comprenant le mélange du composant (a) avec un mélange préformé comprenant les composants (b) et (c).

25 13. Utilisation d'une composition de lubrifiant ou de fluide fonctionnel suivant la revendication 10 ou 11 dans un moyen mécanique, de préférence un moteur à combustion interne ou la transmission d'un véhicule, dans lequel la composition en question est au contact d'une matière élastomérique, notamment d'un élastomère fluoré.

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